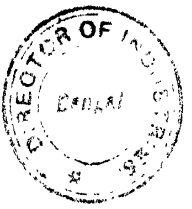


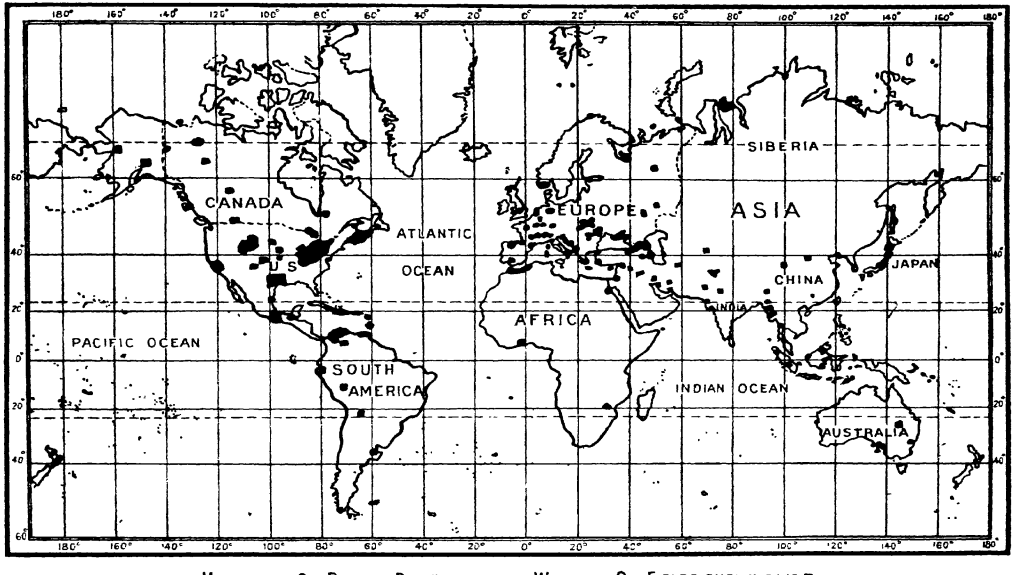
CHEMISTRY OF THE OIL INDUSTRIES

OUTLINES OF INDUSTRIAL CHEMISTRY.

A Series of Text-books Introductory to the Chemistry of the National Industries.

EDITED BY

Guy D. Bengough, M.A., D.Sc.



MAP OF THE OIL BEARING DISTRICTS OF THE WORLD OIL FIELDS SHOWN THUS ■

FIG. 1.

(By permission of Messrs Henry Wells and Scott Tappan)

Frontispiece.

OUTLINES OF INDUSTRIAL CHEMISTRY.

CHEMISTRY OF THE OIL INDUSTRIES

BY

J. E. SOUTHCOMBE, M.Sc.

CHIEF CHEMIST OF THE HENRY WELLS OIL CO., SALFORD; LECTURER ON OILS AND FATS, ROYAL SALFORD TECHNICAL INSTITUTE, ETC.

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DIRECTOR OF INDUSTRIES
Bengal

PREFACE

The extraction of oils and fats from animal and vegetable

ERRATA.

On p. 35 the equation should read

$$C_nH_{2n+2} \longrightarrow C_{(n-1)}H_{2(n-1)} + C_1H_{2\cdot1+2}.$$

On p. 147 the equations should read

$$2C_nH_{2n}(OH).COOR + \begin{matrix} CH_2.O \\ | \\ CH_2.O \end{matrix} \quad O \longrightarrow 2C_nH_{2n}.(OCOCH_3).COOR,$$

and

$$C_nH_{2n}(OCOCH_3).COOR \longrightarrow C_nH_{2n}(OH).COOK + CH_3.COOK + R.OH$$
$$\begin{matrix} \\ | H_2SO_4 \\ CH_3COOH + K_2SO_4 \end{matrix}$$

different oils was obtained and better methods of extracting and refining, as well as preparing finished products from the oil, were consequently evolved. At the present day the importance of chemistry in the oil industry is universally recognised, and the methods of empiricism are rapidly being displaced by the application of chemical laws and principles.

Nevertheless, since many of the chemical and physical forces, which play so important a *rôle* in the technology of oil and its products, are as yet but vaguely understood, many operations in the refinery and particularly the soap works are still conducted on more or less rule of thumb lines. This is due in the main to our comparative ignorance of the influence exerted upon chemical reactions by variations in temperature, pressure, mass and surface action.

Until quite recently, chemists have been occupied chiefly with the analysis, synthesis, and investigation of a vast number of compounds, collecting slowly, but surely, data and evidence, upon which the modern science of Physical Chemistry has been based. This branch of natural philosophy is concerned, as its name implies, with the influence of physical factors on chemical processes, and embraces a still younger science, namely, the study of surface action, which has been called Colloid Chemistry. The progress made in this department of knowledge during the last few years is phenomenal, and already considerable light has been thrown on those obscure phases of oil chemistry of which mention has been made. Indeed, there can be no doubt that a knowledge of this subject will daily become more and more important to the chemical technologist who is concerned with the solution of the multitude of problems in the industry; and there is probably no department of industrial research to-day which offers a wider field for the chemist equipped with the knowledge of physical and organic chemistry than that of oil. Broadly, two distinct branches of chemical science find application in the study of oil - the composition of the bodies constitutes a branch of organic chemistry, while the physical properties and mechanism of the reactions involved belong to physical and colloid chemistry.

In the following pages an attempt is made to indicate in as elementary a manner as possible the general principles of these sciences in so far as they find application in the technology of the oils, fats and waxes.

It will be readily understood that in so small a volume it has been impossible to deal in any way completely with the multitude of facts and theories relative to such an extensive subject, and the object of the work is rather to fill the gap between the elementary text-books of pure chemistry and the numerous technical treatises and monographs of a highly specialised character.

In concluding this preface the author begs to express his indebtedness to the following authorities, upon whom he has in many places drawn freely:-

Ubbelohde—"Handbuch der Öle and Fette," 1908; Lewkowitsch —"Chemical Technology and Analysis of Oils, Fats and Waxes," 1909; Merklen (translated by Goldschmidt)—"Die Kernseifen,"

1907; Redwood—"Petroleum and its Products"; Richter's "Organic Chemistry," and numerous articles in "Journal of the Society of Chemical Industry," "Journal of the Chemical Society, London," "Chemiker Zeitung," "Zeitschrift fur Chemie U. Ind. Kolloide," "Oil and Colour Trade's Journal," "Petroleum Review"; also to Messrs. Geo. Scott and Son, Ltd., Mr. E. Cowles, Messrs. Rose Downs and Thompson, Ltd., Messrs. Henry Wells and Scott Taggart and Messrs. C. Zeiss (London), Ltd., who have kindly lent illustrations, and Mr. A. B. Harris, B.Sc., who has read the proofs.

BIRKENHEAD,
1912.

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CHEMISTRY OF THE OIL INDUSTRIES

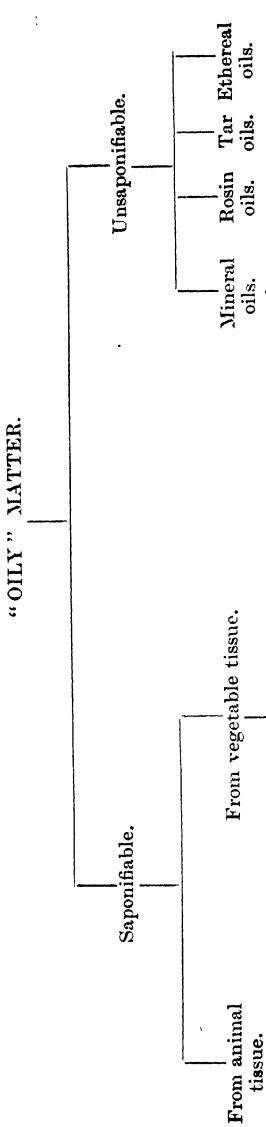
CHAPTER I

INTRODUCTORY ORGANIC CHEMISTRY

The term oil embraces a vast number of substances, both natural and artificial, possessing widely differing chemical composition. All the bodies included in this class are practically insoluble in water, and possess a characteristic greasy touch and low surface tension. To the latter property is due the peculiar ability to spread and penetrate into the pores of dry substances. This forms one of the most distinguishing characteristics of the group, and perhaps in the broadest sense no better definition of an "oil" can be found than that it is "a substance which when dropped upon paper forms a translucent spot which is not removed by washing with water."

When, however, we come to consider the "oils" from the point of view of chemical composition and properties, a sharp line of demarcation is possible, depending upon their behaviour towards boiling solutions of caustic alkalies.

Under the influence of this reagent one large group is split up into two parts, namely, fatty acid and a base (glycerine), and is then said to be "saponified" or "hydrolysed," while the other class remains unaffected. The former, which consist of esters (glycerides), are called "saponifiable," as opposed to the latter "unsaponifiable" oils. This great division may be then divided into several classes, according to the origin of each type, and finally these varieties may again be subdivided in relation to certain physical properties. The following diagrammatic scheme will serve to render this clearer.


"OILY" MATTER.
Saponifiable.
Unsaponifiable.
Mineral oils.
Rosin oils.
Tar oils.
Ethereal oils.
Petroleum and shale.
From animal tissue.
From vegetable tissue.
From marine animals.
From land animals.
Drying oils.
Semi-drying oils.
Non-drying oils.
Solid fats.
Liquid (Oils).
Solid (Fats).

In order to obtain a clear insight into those peculiar properties and reactions which characterise the saponifiable and unsaponifiable oils, one must form a true conception of the nature and structure of the chemical molecule.

The chemistry of the carbon compounds presents a much more involved study of molecular architecture than that of the so-called inorganic compounds, owing to the immense number of widely dissimilar bodies which can be built up from the same two or three elements. When we study the result of analysing a large number of commonly occurring substances, such as sugar, starch, resin, alcohol, fats and oils, we are at once struck with the fact that they all contain only the same three elements, namely, carbon, hydrogen and oxygen. Now the only possible explanation of the fact that substances so dissimilar in their nature and properties as sugar and fat can be formed from the same three elements, is that the atoms of carbon, hydrogen and oxygen are united together in the molecules of sugar in a different way and in different proportions to those in the molecules of a fat. In other words the sugar molecule possesses a different "constitution" to the fat molecule.

A simple analogy will serve to make this conception clearer. With a given number of bricks of different size and shape various buildings may be erected, possessing no similarity in shape or object save that they are all constructed from the same primary material. For example, we might build a castle, chimney, or sewer, entirely with red bricks, yet what could be more dissimilar in appearance or function than a castle and a sewer? Nevertheless when they are broken up the same primary material is obtained from each—a heap of bricks.

So it is with the chemical compounds. The chemical atoms are the bricks, which when built up in various ways give rise to compounds (buildings) differing completely in appearance, properties, and function, yet all composed of the same elementary material, and when decomposed yielding once again these primary constituents. The organic chemist, therefore, must learn to think of sugar as an agglomeration of millions of sugar molecules, each individual being built in a definite form from the three elements carbon, hydrogen and oxygen.

To return to our homely analogy, the bricks require some material to hold them together, and, further, bricks of different shapes and sizes will require varying quantities of mortar. Similarly the atoms are joined in a chemical compound by a binding force, called "chemical affinity," and different atoms require varying quantities of affinity to unite them in a compound. This variation in affinity manifested by the atoms is called the "valency" of the atom, *e.g.*, the hydrogen atom cannot combine with more than one atom of any sort; hence we say that it is "mono" valent, and illustrate it diagrammatically thus, *H*—.

An oxygen atom, however, can combine with two monovalent atoms, which shows that it must possess twice as much affinity as hydrogen; hence we say that oxygen is divalent, and may be represented *O*= or —*O*—.

Similarly nitrogen is trivalent $-N=$ or $-\overset{|}{N}-$ and carbon tetravalent $-\overset{|}{\underset{|}{C}}-$.

Now the explanation of the existence of such a multitude of carbon compounds lies largely in this power possessed by the carbon atoms of combining with four monovalent atoms or groups, and, further, in the fact that the carbon atoms can combine with one another to form long chains or rings.

We usually illustrate this diagrammatically by conceiving the carbon atom as possessing four valencies or "bonds" of affinity radiating out into space thus:—

$$-\overset{|}{\underset{|}{C}}- \text{ or } -\overset{|}{C}= \text{ or } -C\equiv \text{ or } \begin{matrix} C \\ \\ C \end{matrix} \text{ or } C$$

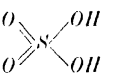
just in the same way as we may consider hydrogen as possessing one "bond," oxygen two, nitrogen three, etc.,

$$H- \quad -O- \quad -N< \quad N\equiv .^{1}$$

Now each of these four free affinities or bonds of carbon may unite with a monovalent element, such as hydrogen, forming the

[1] The student at this stage need not concern himself with the disposition of the bonds in space; it is sufficient to grasp the idea of affinities as represented by the diagrams.

compound CH_4 or $H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$. The formulæ written in the latter way are called constitutional or graphic formulæ, as opposed to the ordinary or empiric formula CH_4, and this applies equally throughout the whole domain of chemistry both inorganic and organic. For example, we may write the formulæ of water, sulphuric acid, caustic potash, etc., in both ways.

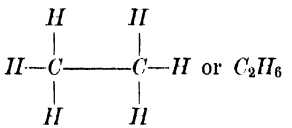
	Empiric Formula.	Graphic or Constitutional Formula.
Water . . .	H_2O	$H-O-H$
Sulphuric acid . .	H_2SO_4	
Caustic potash . .	KOH	$K-O-H$

Now the compound $H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-H$ or CH_4 is a gas known as methane, and is the simplest possible type of organic compound. Methane is the first member of that great class of bodies called "hydrocarbons," because they contain only carbon and hydrogen, and from it all the rest of the organic world can be gradually built up.

Now let us see what could happen if we took away two hydrogen atoms from two molecules of methane, *one from each*. We should get two groups:

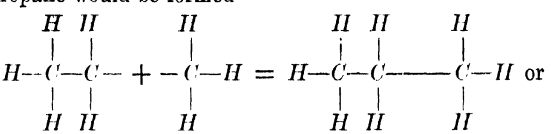
$$\begin{array}{c} H \\ | \\ H-C- \\ | \\ H \end{array} \qquad \begin{array}{c} H \\ | \\ -C-H \\ | \\ H \end{array}$$

each of which would have a free valency, and these two valencies or "rests" would immediately seize each other, giving rise to a new compound



in which the carbon atoms are joined together by a single bond. This compound is also a gas, called ethane.

Similarly, taking a molecule of methane and a molecule of the new compound ethane, and removing a hydrogen atom from each, the same process would take place, and the hydrocarbon propane would be formed



In this way a very large number of carbon atoms may be joined together in a long chain, giving rise to a series of hydrocarbons all modelled on the type of methane.

The table on page 7 gives a list of some of them, and it will be noticed that the empiric formulæ of any two neighbours differ by one carbon and two hydrogen atoms, or CH_2. Such a series, any member of which differs from the preceding one by the constant value CH_2, is called an "homologous" series, and the individual members are called "homologues" of one another.

Further, it will be noticed that since the molecular weight increases by a constant amount for each member, the whole series is capable of being represented by the general formula C_nH_{2n+2}; *i.e.*, if we know that a given member of this series contains six carbon atoms—$n = 6$—we can say at once that it must have fourteen hydrogen atoms ($2 \times 6 + 2$), and its formula is C_6H_{14}.

All these hydrocarbons are very inactive chemically, and so have been called the "paraffin" series.

(Latin—*parum affinis* = little affinity).

SATURATED HYDROCARBONS (PARAFFIN SERIES) (NORMAL). (RICHTER.)

Formula.	Name.	Melting Point °C.	Boiling Point °C	
CH_4	Methane	—	Gas	
C_2H_6 or $CH_3.CH_3$[1]	Ethane	—	Gas	
C_3H_8 or $CH_3.CH_2.CH_3$	Propane	—	—	
C_4H_{10} or $CH_3.CH_2.CH_2.CH_3$	Normal Butane	—	+ 1 (B. 27, 2768)	
C_5H_{12} or $CH_3(CH_2)_3CH_3$	Normal Pentane	—	+ 38	
C_6H_{14} or $CH_3.(CH_2)_4.CH_3$	Normal Hexane	—	+ 71	
C_7H_{16}	Heptane	—	98·4	
C_8H_{18}	Octane	—	125·5	
C_9H_{20}	Nonane	− 51	149·5	
$C_{10}H_{22}$	Decane	− 32	173	under 760 m.m. pressure.
$C_{11}H_{24}$	Undecane	− 26·5	194·5	
$C_{12}H_{26}$	Dodecane	− 12	214	
$C_{13}H_{28}$	Tridecane	− 6·2	234	
$C_{14}H_{30}$	Tetradecane	+ 5·5	252·5	
$C_{15}H_{32}$	Pentadecane	+ 10	270·5	
$C_{16}H_{34}$	Hexadecane	+ 18	287·5	
$C_{17}H_{36}$	Heptadecane	+ 22·5	303	
$C_{18}H_{38}$	Octadecane	+ 28	317	
$C_{19}H_{40}$	Nonadecane	+ 32	330	
$C_{20}H_{42}$	Eicosane	+ 36·7	205	under 15 m.m. pressure.
$C_{21}H_{44}$	Heneicosane	+ 40·4	215	
$C_{22}H_{46}$	Docosane	+ 44·4	224·5	
$C_{23}H_{48}$	Tricosane	+ 47·7	234	
$C_{24}H_{50}$	Tetracosane	+ 51·1	243	
$C_{27}H_{56}$	Heptacosane	+ 59·5	270	
$C_{31}H_{64}$	Hentriacontane	+ 68·1	302	
$C_{32}H_{66}$	Dotriacontane	+ 70	310	
$C_{35}H_{72}$	Pentatriacontane	+ 74·7	331	
$C_{30}H_{122}$	Dimyricyl	+ 102	—	

Each of these compounds may be looked upon as formed by the union of two hydrocarbon molecules, from each of which one *H* atom has been removed, leaving a free rest or valency. Such rests are called radicles, and are usually designated by changing the final syllable of the hydrocarbon into *yl*. Thus methane less one *H* atom forms the radicle named "methyl" $H-\overset{H}{\underset{H}{C}}-$.

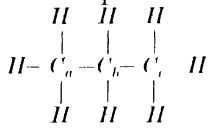
Ethane less one *H* atom is called "ethyl" C_2H_5. Similarly we get C_3H_7—propyl, C_4H_9—butyl, etc. We may now say that the

[1] For convenience and economy of space it is usual to write graphic formulæ simply showing each *C* atom and the atoms to which it is joined without putting in the linkages.

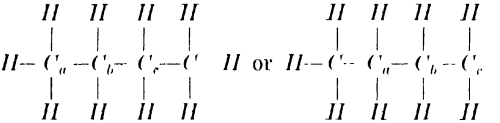
union of two methyl groups forms ethane—of one methyl and one ethyl, propane, etc.

Now when we consider the formation of C_4H_{10} by substitution of one of the hydrogen atoms of propane by methyl, we see that there will be a difference in the structure of the butane formed, according to which of the hydrogen atoms of propane are replaced. This is best seen from the diagram

Propane.

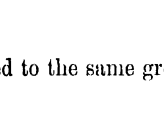


It is obvious that the replacement of either of the hydrogen atoms joined to a or c will give rise to identically the same compound,



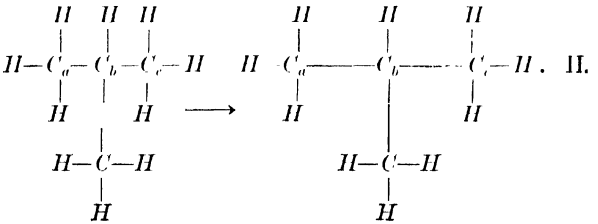
. I.

since the two end carbon atoms are equivalent, being both



joined to the same group—in a perfectly symmetrical way.

If, however, a hydrogen atom attached to b is removed, a different compound is formed, viz.



. II.

The structural difference is readily seen by writing them in the abbreviated way, thus:

Substitution of a hydrogen atom attached to either *a* or *c* gives:

$$CH_3.CH_2.CH_2.CH_3 \quad . \quad . \quad . \quad . \quad \text{I.}$$

Substitution of a hydrogen atom attached to *b* gives,

$$CH_3.CH\begin{matrix}CH_3\\CH_3\end{matrix} \quad . \quad . \quad . \quad . \quad \text{II.}$$

Such compounds, possessing identical empiric formulæ but differently arranged atomic structure, are termed "isomers." The straight chain structure is called the "normal," while the side chain compound is called the "isomeric" or "iso" form. It is evident that no isomers can be formed by the first three paraffins, since the structure is perfectly symmetrical. Two butanes, three pentanes, five hexanes, and, when we come to the paraffins of eight carbon atoms, eighteen isomers are possible, most of which are known. These isomeric forms are similar in chemical properties, but differ in their physical deportment, such as freezing point, boiling point, etc.

The following table illustrates this peculiarity:—

TABLE OF ISOMERIC PARAFFINS.

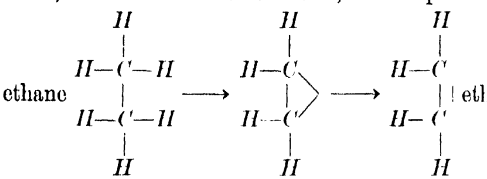
Empiric Formula.	Constitutional Formula.	Name.	Boiling Point C.
C_4H_{10} . .	(Normal) $CH_3.CH_2.CH_2.CH_3$. (Iso) $CH_3.CH(CH_3).CH_3$	Normal Butane Isobutane	+ 1 − 17
C_5H_{12} . .	(Normal) $CH_3.CH_2.CH_2.CH_2.CH_3$ (Iso) (1) $CH_3.CH(CH_3).CH_2.CH_3$.	Normal Pentane Isopentane	+ 38 + 30
	(2) $CH_3-C(CH_3)_2-CH_3$	Tetramethyl Methane	+ 10

This phenomenon of isomerism is very common in organic chemistry, nearly all compounds possessing isomeric relationship.

The particular kind of isomerism mentioned above is due to the different structure of the chain of carbon atoms, and is

therefore called "structural" or "nuclear" isomerism. Later on we shall see that other types of isomerism exist.

If two hydrogen atoms are removed from any two *adjacent* carbon atoms in a saturated hydrocarbon, the two free valencies thus formed immediately unite to form a compound in which these two particular carbon atoms are joined by a double bond. Thus in the case of ethane we get, by removing any two hydrogen atoms, one from each carbon atom, the compound ethylene.



This gives rise to another series of hydrocarbons, called the olefines, and since these bodies are chemically very reactive, adding on two atoms of hydrogen, chlorine or bromine, etc., with avidity, they are called "unsaturated hydrocarbons."

Every paraffin or saturated hydrocarbon, open chain or iso, has its corresponding olefine, which may be considered as being derived, as before mentioned, by simple removal of one hydrogen atom each from any two adjacent carbon atoms in a saturated hydrocarbon.

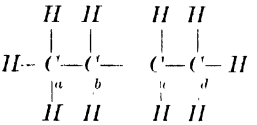
TABLE SHOWING A FEW OLEFINES AND THEIR RELATIONSHIP TO CORRESPONDING PARAFFINS.

Saturated or Paraffin Hydrocarbon.	Corresponding Olefine.	Boiling Point °C.
Ethane $CH_3.CH_3$	Ethylene $CH_2 \quad CH_2$	Gas
Propane $CH_3.CH_2.CH_3$	Propylene $CH_3.CH = CH_2$	− 40 (gas)
Butane $CH_3.CH_2.CH_2.CH_3$	Butylene $CH_3.CH_2.CH = CH_2$	− 5
	or $CH_3.CH = CH — CH_3$ [1]	+ 1
Isobutane $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH — CH_3$	Isobutylene $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C = CH_2$	− 6
Pentane $CH_3.CH_2.CH_2.CH_2\,CH_3$	Pentylene or Amylene $CH_3.CH_2.CH_2CH = CH_2$	+ 39
Isopentane $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH — CH_2.CH_3$	Isoamylene $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH — CH = CH_2$	+ 21

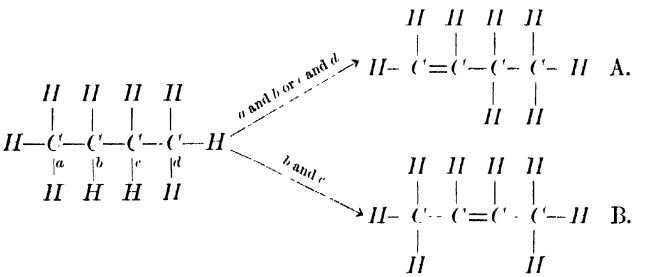
[1] Positional Isomer.

A study of the table will show that, like the paraffins, the olefines form an homologous series, but of the general formula C_nH_{2n}.

Now, suppose we took butane, and decided to remove two hydrogen atoms, one from each of two neighbouring carbon atoms, as above described, we see at once that in this case there is a choice of which two carbon atoms shall be deprived of hydrogen.



We might take away a hydrogen atom each from a and b, b and c, or c and d. Now the carbon atoms a and d are exactly similar, as also are b and c, since in both cases they are joined in the same way. To make this clearer, suppose we divided the formula by a plane between the carbon atoms b and c. Two halves would be left, exactly similar in all respects, viz., CH_3—CH_2. In other words, the structure of the molecule is symmetrical. From this is clear that it is immaterial whether the hydrogens be removed from a and b or c and d, since the same compound would result in either case. If, however, the hydrogen atoms joined to b and c were removed, a totally different structure would be obtained. This is readily seen from the diagram.



This again is an example of isomerism. The two compounds A. and B. being isomers of one another. In this case, however, contrary to the isomerism of the saturated hydrocarbons, there is no difference between the structure of the carbon chain in

either case, *i.e.*, both are straight open chains, the only difference arising from the varying positions of the double bonds.

For this reason the phenomenon is spoken of as "positional isomerism." It is clear that as the number of carbon atoms in the molecule increases, the number of isomers corresponding to any given empiric formula becomes larger. For example, C_4H_8 has only two possible positional isomers, while $C_{20}H_{40}$ may have nine different forms, according to the position of the double bonds. Consequently it becomes necessary to have some simple nomenclature. This is usually done by numbering the carbon atoms in the chain, and in the case of those compounds possessing side chains, always choosing the longest string of carbons.

The double bond may then be indicated by referring to the number of the carbon atom to which it is joined.

$$\begin{array}{cc} 1\ 2\ 3 & 4\ 5\ 6 \\ CH_3.CH_2.CH=CH.CH_2.CH_3 \\ 6\ 5\ 4 & 3\ 2\ 1 \end{array}$$

A.

Compound A. on this system is called 3 hexylene:

Further, we may have a combination of nuclear and positional isomerism, since the unsaturated part of the molecule may possess side chains. An example will make this clear. A compound C_5H_{10} may be written $CH_3.CH_2.CH = CH.CH_3$

or $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH - CH_2$, etc.

The student is advised to take any empiric formula, say $C_{20}H_{40}$, and work out for himself all the possible arrangements of 20 carbon atoms and 40 hydrogen atoms which can be made to fit these conditions. We will now pass on to consider another great series of unsaturated derivatives. Just in the same way as described above for paraffins, the removal of two hydrogen atoms from neighbouring carbon atoms in an olefine gives rise to a compound containing a triple bond.

This is the most unsaturated type of organic compound possible, and is known as the acetylene series.

Ethylene, for example, gives acetylene

$$\begin{matrix} H-C=C-H \\ \quad|\quad| \\ \quad H\quad H \end{matrix} \quad \text{minus 2 } H \longrightarrow H-C\equiv C-H \text{ or } C_2H_2$$

a highly inflammable gas, which is the simplest member of the series. The names of the hydrocarbons of this series are formed by the suffix "ine" so that scientifically, acetylene should be called "ethine," thus distinguishing it from its two relatives, ethene or ethylene C_2H_4, ethane C_2H_6.

TABLE OF ACETYLENE HYDROCARBONS

Empirical Formula.	Constitutional Formula	Name.	Boiling Point C
C_2H_2	$CH \equiv CH$	Acetylene	Gas.
C_3H_4	$CH_3 - C \equiv CH$ (1 2 3 4)	Allylene or Propine	Gas.
C_4H_6	(1) $CH_3 - C \equiv C - CH_3$ (1 2 3 4)	Crotonylene or 2 Butine	27—28
	(2) $CH_3 CH_2 - C \equiv CH$ (1 2 3 4 5)	Ethyl acetylene or 3 Butine	18
C_5H_8	(1) $CH_3 CH_2 CH_2 - C \equiv CH$ (1 2 3 4)	Propyl acetylene or 4 Pentine	48—49
	(2) $CH_3 - CH(CH_3) - C \equiv CH$ (1 2 3 4)	Isopropyl acetylene or 2 Methyl Butine	28 29
	(3) $CH_3 CH_2 - C \equiv C - CH_3$ (1 2 3 4 5)	Methyl ethyl acetylene or 3 Pentine	55—56

General Formula of the series C_nH_{2n-2}.

Both nuclear and positional isomerism is found in the acetylene series. A few of the isomeric forms known are given in the table.

The triple bond hydrocarbons are intensely active chemically, combining with chlorine, bromine, etc., with explosive violence. The compounds may take up either two or four hydrogen atoms, forming olefine or paraffins respectively. In this way we see the relationship of these great series very clearly.

$$\underset{\text{Acetylene}}{CH \equiv CH} + 2H \longrightarrow \underset{\text{Ethylene}}{CH_2 = CH_2} \xrightarrow{2H} \underset{\text{Ethane}}{CH_3 - CH_3}$$

It must not be thought that a double or triple union between two carbon atoms confers extra strength on the molecule.

On the contrary, a double or triple union is much weaker than a single union, and if an unsaturated compound be subjected to

any powerful chemical influences tending to decomposition, *e.g.*, strong oxidising agents, it is the unsaturated linkage which breaks first. This is found to be the case in all organic compounds, the decomposition of the most complex molecules always resulting ultimately in the formation, in greater or less quantity, of saturated hydrocarbons, and particularly of methane.

It is, however, this extremely stable nature of the saturated compounds which renders them so remarkably inert in their chemical properties, and were it not for the existence of the more reactive double bonds, organic chemistry would not be nearly so fertile a study as it is.

The three series of hydrocarbons just described are all constructed on an open chain model, *i.e.*, their nucleus consists of a long string of carbon atoms joined together as a chain; and since the fats are known to be constituted in a similar way, and further, as many of these hydrocarbons can be obtained from the fats by certain chemical processes, they have been called the "aliphatic" group of hydrocarbons. The paraffins, olefines and acetylenes are the primary types, but many other compounds are known, built up of a combination of one or more of these varieties.

The union of two olefine "rests" produces a compound containing two double bonds in the chain, called "diolefines."

Two ethylene molecules, for example, each deprived of one hydrogen atom, or, as we say, two ethylene radicals, yield "divinyl."

$$CH_2{=}CH{-}\quad{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH_2.$$
$$+$$

Similarly from propylene we get "diallyl"

$$2\,CH_3{-}CH{=}CH{-} \longrightarrow CH_3{-}CH{=}CH{-}CH{=}CH{-}CH_3$$

which also may exist in an isomeric form.

A considerable number of the members of this homologous group are known, but they are comparatively unimportant. The general formula of the group is C_nH_{2n-2}. They are all isomeric with the acetylene hydrocarbons. Divinyl C_4H_6, for example, has the same empiric composition as crotonylene, $CH_3{-}C{\equiv}C{-}CH_3$.

A few of the better known diolefines are:

Empiric Formula.	Constitutional Formula.	Name.	Boiling Point °C.
C_3H_4	$CH_2=C=CH_2$	Allene	Gas
C_4H_6	$CH_2=CH-CH=CH_2$	Divinyl	,,
C_5H_8	$CH_2-CH-CH_2-CH=CH_2$	Piperylene	42
C_6H_{10}	$CH_2=CH-CH_2-CH_2-CH=CH_2$	Diallyl	59·3

Again an olefine rest may unite with an acetylene rest, giving a compound containing both a double and a triple bond in the chain

$$CH_2=CH-C\equiv CH.$$

Only a few of the members of this series are known, and it is unnecessary to describe them here.

Finally, two acetylene rests give rise to the diacetylenes, many representatives of which series are known.

Diacetylene, $CH\equiv C-C\equiv CH$, is a gas.

Dipropargyl, $CH\equiv C-CH_2-C\equiv CH$, is a liquid boiling at 85° C.

The above examples will serve to show how the complex hydrocarbons are built up, and the reader will see that an endless variety of hydrocarbons can be theoretically constructed by combining together the three primary rests (paraffin, olefine and acetylene) in various ways, and, so to speak, ringing the changes. One has only to bear in mind that each carbon atom must have four valencies accounted for in some way, and that the disposition of these valencies is such that a complete chain of combinations is formed, in order to construct all manner of theoretically possible compounds. Many hundreds of these theoretical predictions are known, and probably within certain limits all may be synthesised or discovered. At any rate, it is highly probable that in the naturally occurring product called petroleum a large number of these complicated types occur, and, notwithstanding the multitudes which have already been isolated, yet others remain to be discovered.

The reader will find it a most attractive study to write out a number of possible types. It will be observed that there is no

apparent end to the degree of unsaturation obtainable, a gradual diminution in hydrogen content being possible, probably even until pure carbon is reached.

Hydrocarbons containing as many as six double bonds have been prepared and found to be highly unstable explosive bodies.

Further, the nature of the compounds of low hydrogen percentage found in natural petroleum and asphalte, although quite unknown at present, must undoubtedly be built up on some system such as we have outlined. It is even doubtful whether we have ever yet obtained pure carbon. Lamp black and sugar charcoal, generally supposed to be pure forms of carbon, always contain a minute percentage of hydrogen, and the diamond is never free from ash.

So far we have only considered those compounds which possess an open chain structure. There exists, however, another great division of organic chemistry, viz., the "cyclic" or "aromatic" group, which again has for its parent the aromatic or ring hydrocarbon.

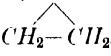
It was stated on page 7 that when a hydrogen atom is abstracted from the formula of any hydrocarbon a monovalent group is left. Thus $CH_4—H \longrightarrow CH_3—$.

By the removal of two hydrogen atoms a divalent group results.

Thus CH_4 gives CH_2 = called methylene.

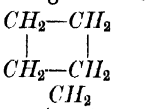
Groups like these which deport themselves like individual atoms, are called "radicals." The number of radicals known is very great, and they may all be considered as derived from some compound by the removal of one or more atoms.

Consider the grouping $—CH_2—CH_2—CH_2—$. The two end methylene groups ($—CH_2—$) each possess a free bond; but we have seen that free bonds can unite with one another quite readily, hence it is clearly possible that the two unattached links in the above group can be attracted to one another, join up and so form a "ring" of carbon atoms thus,

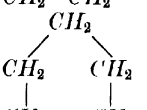


Such compounds are known, and are called cyclo-paraffins or naphthenes. This particular one is a gas, and since it contains

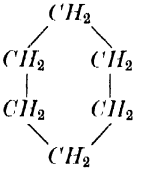
three methylene groups is called trimethylene, and is typical of a three-membered ring. Four, five, six, seven, and eight-membered rings are known, namely:



Tetramethylene or cyclobutane.[1]

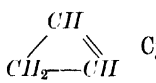


Pentamethylene or cyclopentane.

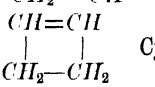


Hexamethylene or cyclohexane.

These bodies have the same general formula as the olefines. They possess, however, no double bond, and so owing to their saturated structure they are much more stable and differ widely from the olefines. Exactly as with the open chain hydrocarbons, hydrogen can be abstracted from these and unsaturated rings formed. Thus:

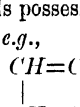


Cyclopropene from cyclopropane.



Cyclobutene from cyclobutane.

The compounds possessing two double links are named by the suffix "diene"; *e.g.*,

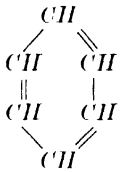


cyclobutadiene.

When six hydrogen atoms are removed from the six-membered ring cyclohexane, a hydrocarbon is obtained possessing three double bonds, but yet of great stability. It is "benzene," an important constituent of coal-tar.

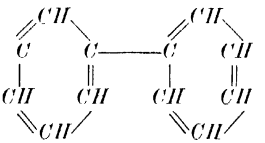
[1] An alternative nomenclature for this series is arrived at by prefixing the word cyclo to the name of the open chain paraffin containing the same number of carbon atoms. On this system trimethylene would be called cyclopropane.

The formula of benzene is written:

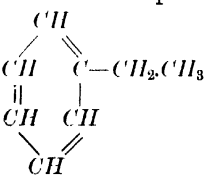


Benzene is a volatile liquid boiling at 85° C., and occurs in considerable quantity in the products of distillation of coal. It is by far the most important hydrocarbon known because it can be transformed into a great variety of valuable compounds by acting upon it with reagents. Benzene is the simplest member of a great series of hydrocarbons known as the "aromatic" group, the detailed consideration of which, however, falls outside the scope of this book, as they do not occur to any great extent in the natural oils or fats.

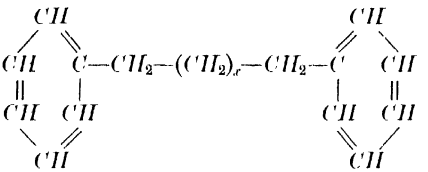
The ring hydrocarbons may unite with themselves and with open chains in endless variety, from which the reader will see that the number of theoretical possibilities is almost infinite. A benzene molecule minus one hydrogen atom constitutes the hypothetical radical phenyl C_6H_5- and two phenyls may unite to form a compound containing two rings called diphenyl $C_6H_5 \ C_6H_5$,



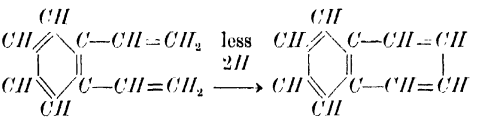
So the rings are united. Further the ring radical may join with an open chain radical; thus phenyl can combine with ethyl, the compounds so produced being called "alkylated rings," partake of the properties of both aliphatic and aromatic series.



Such a compound as that last mentioned is sometimes found with the aliphatic side chain joined to another ring, and so we get the following type:



A very well known and important compound is built up by replacing two adjacent hydrogen atoms in the benzine ring by ethylene radicals, and then removing one hydrogen atom from each of the CH_2 groups of the side chain. This compound is known as naphthalene, an important solid constituent of coal-tar.



We have now outlined briefly and in the simplest possible manner the broad theoretical principles upon which the conception of carbon chemistry is based. The principles of constitutional structure have been explained, and the system upon which the most complex hydrocarbon is built has been described. No attempt has been made to indicate the methods employed in the laboratory to synthesise or isolate these compounds or bring about the remarkable reactions which have been theoretically postulated. It will be sufficient to point out, however, that although large numbers of compounds of this type have been prepared, yet many remain to be discovered, and there is no doubt that in the natural product known as petroleum a vast storehouse of hydrocarbons of the most complex type is at hand; and rapid as the progress has been during recent years in the elucidation of its composition, there remains a wide field for the organic chemist who shall separate from it and demonstrate the constitution of numbers of these as yet unknown hydrocarbons.

The hydrocarbons have been described as the parents of the

organic compounds, since from them all the known types of carbon compounds may be theoretically derived by the substitution of oxygen, nitrogen, sulphur, phosphorus and halogens for one or more hydrogen atoms in the molecule.

We shall now pass on to consider those particular oxygenated carbon compounds which are of interest to the oil chemist. They are chiefly the alcohols, aldehydes, ketones and carboxylic acids, all of which may be considered as derived from some parent hydrocarbon by the substitution of one or more of its hydrogen atoms by definite groupings or radicals. Four such groupings or radicals are:

(*a*) The hydroxyl group OH which may be looked upon as a molecule of water HOH minus one hydrogen atom.

(*b*) The aldehyde grouping $C\begin{matrix}\diagup\!\!\!\!\diagup O \\ \diagdown H\end{matrix}$ or CHO, which may be considered as an alcohol grouping minus the elements of water.

(*c*) The ketone radical $= CO$.

(*d*) The carboxyl group $- COOH$.

Alcohols.—When one of the hydrogen atoms of any hydrocarbon is replaced by the hydroxyl group, an "alcohol" is formed; thus from

Methane CH_4 methyl alcohol CH_3OH,
Ethane C_2H_6, ethyl alcohol, C_2H_5OH,

and so on.

The alcohols formed in this manner and containing only one hydroxyl group are known as "monohydric" alcohols, the most important representative of which is the ethyl homologue or ordinary alcohol obtained by the fermentation of carbohydrate materials. The saturated monohydric alcohols form an homologous series of general formula $C_nH_{2n+1}OH$. A few of the better known members are here given.

Hydroxyl derivatives of the aromatic hydrocarbons are also of great importance. The best known is phenol, or carbolic acid. Its constitutional formula is

$$\underset{\text{benzene}}{C_6H_6} \longrightarrow \underset{\text{phenol.}}{C_6H_5OH}$$

MONOHYDRIC ALCOHOLS OF THE SATURATED SERIES.

Parent Hydrocarbon.	Corresponding Alcohol.	Name.	Boiling point at 760 millimetres. °C.
Methane . .	$CH_3.OH$	Normal Methyl	66/67
Ethane . .	$CH_3.CH_2.OH$	Ethyl	78·3
Propane . .	$CH_3.CH_2.CH_2.OH$	Propyl	97
,, . .	$CH_3.CH(OH).CH_3$	Isopropyl	82·7
Butane . .	$CH_2.CH_2.CH_2.CH_2\ OH$	Normal butyl	116·8
,, . .	$(CH_3)_2.CH.CH_2.OH$	Isobutyl	108·4
,, . .	$CH_3.CH_2 \rangle CH.OH$ CH_3	Secondary butyl	99
,, . .	$(CH_3)_3C.OH$	Tertiary butyl	83
Pentane . .	$CH_3.(CH_2)_3.CH_2.OH$	Normal amyl	137
,, . .	CH_3 $CH_3.CH_2 \rangle {}^{1}CH.CH_2.OH$	Active amyl	128·7
Hexadecane .	$CH_3.(CH_2)_{14}.CH_2.OH$	Cetyl	340
Heptacosane .	$C_{26}H_{53}.OH$	Ceryl	
Triacontane .	$C_{30}H_{61}\ OH$	Myricyl	

The aromatic alcohols, however, are rarely found in the fats and oils, and so we shall not consider them here.

Positional and nuclear isomerism occurs in these compounds also, each isomeric form of the hydrocarbon having its corresponding alcohol, thus:

Positional Isomerism.	Nuclear Isomerism.
CH_3 $\quad$ CH_3 $\vert$ $\quad$ $\vert$ CH_2 and $CH-OH$ $\vert$ $\quad$ $\vert$ CH_2OH $\quad$ CH_3	CH_3 $\quad$ CH_3 $\vert$ $\quad$ $\rangle$ CH_2 and $CH.CH_2OH$ $\vert$ $\quad$ CH_3 CH_2 $\vert$ CH_2OH

Hydroxyl derivatives of the unsaturated hydrocarbons are also known, but are of less importance than those of the saturated group. A typical member is allyl alcohol $CH_3.CH=CH.OH$.

Alcohols formed by the substitution of two or more hydrogen atoms of a hydrocarbon by OH are called "polyhydric" alcohols.

The trihydric obtained by replacing three hydrogen atoms, one from each carbon atom in propane, is known as glycerol.

The open chain or aliphatic alcohols are basic, the hydrogen

[1] Assymetric carbon atom

atom of the hydroxyl group being replaceable by metals. We may therefore speak of the alcohols as mono- di- or tri-basic, according as they contain one, two or three hydroxyl groups.

When two or more hydrogen atoms attached to different carbon atoms are replaced by hydroxyl, the alcohols formed are called di, tri, tetra, penta, and hexa hydric alcohols respectively.

The alcohols are indicated by the termination ol.

As types of polyhydric alcohols may be mentioned :

Glycol.	Glycerol.	Erythritol.	Arabitol.	Mannitol.
$CH_2.OH$	$CH_2.OH$	$CH_2.OH$	$CH_2.OH$	$CH_2.OH$
$CH_2.OH$	$CH.OH$	$CH.OH$	$CH.OH$	$CH.OH$
	$CH_2.OH$	$CH.OH$	$CH.OH$	$CH.OH$
		$CH_2.OH$	$CH.OH$	$CH.OH$
			$CH_2.OH$	$CH.OH$
				$CH_2.OH$
	occurs in fats and oils.	in seaweeds.	in gum arabic?	in manna.

The accumulation of OH groups in a compound, renders it more soluble in water and sweetish in taste. The sugars are derivatives of the penta and hexa hydric alcohols.

Aldehydes.

When alcohols are subjected to the action of oxidising agents under certain conditions, the elements of water are eliminated from the alcohol and an oxygen atom taken up, according to the following equation :

$$CH_3-\overset{H}{\underset{H}{C}}-OH \xrightarrow{+O} CH_3.C\overset{O}{\underset{H}{<}} + HOH$$

ethylalcohol. acetaldehyde.

The new body formed is called an "aldehyde" (Latin, *Alcohol dehydrogenatum*). The aldehydes are the first products of the oxidation of alcohols. They all contain the group

$$-C\begin{matrix}H\\ \diagdown\!\!\!\!\diagup\\ O\end{matrix} \quad \text{or simply} \quad -CHO.$$

called the aldehyde grouping.

The aldehydes are characterised by very penetrating odours, those formed from the lower alcohols being very pungent and volatile. They are all powerful reducing agents.

As every hydrocarbon has its corresponding alcohol, so every alcohol has its related aldehyde. Aldehydes formed from the unsaturated alcohols are also known. The most important of these is acrolein, $CH_2{=}CH.CHO$, since it is invariably produced when fats are decomposed by heat. The aldehyde is generated from the glycerol half of the fat molecule

$$\begin{matrix}CH_2.OH\\ |\\ CH.OH\\ |\\ CH_2.OH\end{matrix} \xrightarrow{O} \begin{matrix}CH_2\\ \|\\ CH\\ |\\ CHO\end{matrix}$$

Ketones.

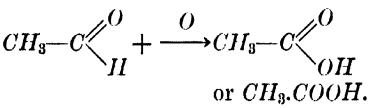
Closely related to the aldehydes, but of somewhat less importance to the oil chemist, are the ketones. These bodies are produced by the oxidation of alcohols of three or more carbon atoms containing the hydroxyl group attached to an *intermediate* carbon atom. Thus, iso propyl alcohol gives on oxidation acetone.

$$\begin{matrix}CH_3\\ |\\ CH.OH\\ |\\ CH_3\end{matrix} \xrightarrow{O} \begin{matrix}CH_3\\ |\\ C{=}O\\ |\\ CH_3\end{matrix}$$

Acids.

We have seen that the oxidation of an alcohol under certain conditions gives rise to either an aldehyde or a ketone, according as the hydroxyl group is joined to an end or an intermediate carbon atom. If now an aldehyde be still further oxidised, it passes into an acid.

Acetaldehyde gives acetic acid.

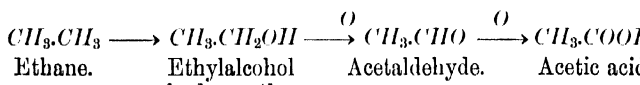


or $CH_3.COOH$.

The acids form one of the most important groups of organic compounds, and are always the ultimate oxidation product of an alcohol. The aliphatic acids are built up on the type $R.COOH$.

The group $C.OOH$ which persists in them throughout is known as "Carboxyl," and the acids therefore are generally called "carboxylic acids." Those formed from the monohydric alcohols and containing therefore one carboxyl group, are termed "fatty acids," because many of them occur in fats and oils.

The relationship of all these compounds to one another and their parent hydrocarbon is clearly seen in the scheme below



Ethane. Ethylalcohol or hydroxyethane. Acetaldehyde. Acetic acid.

Substitution of one hydrogen atom of the hydrocarbon by OH gives rise to a monohydric alcohol, which on mild oxidation passes into the aldehyde and finally, by more vigorous oxidation, into the corresponding monocarboxylic or fatty acid.

Those acids which are derived from the paraffin series of hydrocarbons are called "saturated acids," while those obtained from the olefine or acetylene series are termed the "unsaturated acids."

The saturated or fatty acids form an homologous series of formula $C_nH_{2n+1}COOH$. The lower members are pungent, volatile liquids of strong acid properties, while the higher members are crystalline solids, possessing but feeble acidity.

The saturated fatty acids are chemically very stable. At ordinary temperatures they are unaffected by air or halogens, but when heated to a high temperature they decompose, with the formation of CO_2, methane and other hydrocarbons. They all form salts with the metals.

The sodium salts, when treated with soda lime, lose the carboxyl group, giving rise to paraffin hydrocarbons.

The table gives a few of the more important acids of normal structure.

MONOBASIC SATURATED ACIDS (NORMAL).

Parent Hydrocarbon.	Acid.	Melting Point. °C.	Boiling Point. °C.	
Methane CH_4	Formic $H.COOH$	+ 8	100·5	
Ethane C_2H_6	Acetic $CH_3.COOH$	16·7	118·0	
Propane C_3H_8	Propionic $C_2H_5.COOH$	−36	140·0	
Butane C_4H_{10}	Butyric $C_3H_7.COOH$	− 4	163·0	
Pentane C_5H_{12}	Valeric $C_4H_9.COOH$	−59	186·0	
Hexane C_6H_{14}	Caproic $C_5H_{11}.COOH$	− 8	205	760 millimetres.
Heptane C_7H_{16}	Oenanthylic $C_6H_{13}.COOH$	−10·5	223	
Octane C_8H_{18}	Caprylic $C_7H_{15}.COOH$	16·5	237	
Nonane C_9H_{20}	Pelargonic $C_8H_{17}.COOH$	12·5	254	
Decane $C_{10}H_{22}$	Capric $C_9H_{19}.COOH$	31·4	270	
Undecane $C_{11}H_{24}$	Undecylic $C_{10}H_{21}.COOH$	28·5	(212·5)	100 millimetres.
Dodecane $C_{12}H_{26}$	Laurie $C_{11}H_{23}.COOH$	43·5	(227·5)	
Tridecane $C_{13}H_{28}$	Trydecylic $C_{12}H_{25}.COOH$	40·5	(236)	
Tetradecane $C_{14}H_{30}$	Myristic $C_{13}H_{27}.COOH$	53·8	(250·5)	
Hexadecane $C_{16}H_{34}$	Palmitic $C_{15}H_{31}.COOH$	63	(271·5)	
Octodecane $C_{18}H_{38}$	Stearic $C_{17}H_{35}.COOH$	69·2	(291)	
Eicosane $C_{20}H_{42}$	Arachidic $C_{19}H_{39}.COOH$	75	—	
Pentacosane $C_{25}H_{52}$	Cerotic $C_{24}H_{49}.COOH$	78	—	
Triacontane $C_{30}H_{62}$	Melissic $C_{29}H_{59}.COOH$	90	—	

The carboxylic acids derived from olefine or unsaturated hydrocarbons are, on the contrary, very reactive, as is to be expected from the presence of the double bond.

The best-known members of the series containing one double bond in the carbon chain, are:—

UNSATURATED MONOBASIC ACIDS CONTAINING ONE DOUBLE BOND.

Acid	Melting Point °C	Boiling Point °C.
Acrylic $CH_2=CH.COOH$	7·0	140
Crotonic $CH_3.CH=CH.COOH$	72	180
Tiglic $CH_3.CH=C(CH_3)-COOH$	64·5	198
Nonylenic $CH_3(CH_2)_5.CH=CH.COOH$		
Undecylenic $CH_2=CH-(CH_2)_8.COOH$	24·5	165 (15 millimetres)
Oleic $C_8H_{17}.CH=CH(CH_2)_7.COOH$	14	223 (10 millimetres)
Rapic $C_{17}H_{33}COOH$	—	—
Erucic $C_{21}H_{41}COOH$	33·5	281 (30 millimetres)

Carboxylic acids possessing a triple bond in the chain corresponding to the acetylene series are not known with certainty,

but many acids occurring in natural oils contain two or more double bonds, derived from diolefine hydrocarbons, etc.

Such acids are much more reactive chemically than those containing only one double linkage. They rapidly absorb oxygen from the air and combine vigorously with halogens.

The ability to combine with bromine or iodine presents a most valuable means of ascertaining their presence in admixture with saturated acids, both qualitatively and quantitatively. The number of grammes of iodine or bromine with which 100 grammes of the oil can combine, is called in fat analysis the iodine or bromine absorption figure, of which more will be said under the heading "Analytical Methods."

One of the most delicate tests for detecting the presence of a double bond in an aliphatic chain is the power of decolourising a solution of potassium permanganate, and is known as Bayer's test. If an unsaturated acid be shaken with a few drops of alkaline permanganate solution, the acid becomes converted into an hydroxyacid, and the permanganate is at the same time de-colourised.

The exact structure of many of these highly unsaturated acids is unknown, since they manifest such a strong affinity for oxygen and are chemically so unstable that their investigation is a matter of extreme difficulty. It is probable, however, that very highly unsaturated acids occur in some of the fish-liver oils.

It was pointed out when studying the hydrocarbons that the addition of pairs of hydrogen atoms to unsaturated compounds gives rise theoretically to more saturated derivatives containing the same number of carbon atoms. Similar relations are found among the acids. Starting with an acid containing, say, two double bonds, and adding two hydrogen atoms, we get the corresponding compound which possesses only one double bond, and this, in turn, with two more hydrogens, passes into the fully reduced or saturated acid. The unsaturated linkage always tends to become saturated. An example will make this clearer.

$$\underset{\text{Linolic acid}}{C_{17}H_{31}.COOH} \xrightarrow{+2H} \underset{\text{Oleic acid}}{C_{17}H_{33}.COOH} \xrightarrow{+2H} \underset{\text{Stearic acid.}}{C_{17}H_{35}.COOH}$$

In the same way, an unsaturated acid can combine with a

halogen to form saturated addition products. The addition of two halogen atoms takes place at each double bond. So, for example, oleic acid combines with bromine, forming dibromstearic, $C_{17}H_{33}Br_2 . COOH$, while linolic takes up four atoms of bromine to form tetrabromstearic, $C_{17}H_{31}Br_4COOH$.

Now when these brom compounds are boiled with a solution of caustic potash in water, the two bromine atoms are removed, and hydroxyl groups take their place.

$$C_{17}H_{33}Br_2.COOH + \xrightarrow{2KOH} C_{17}H_{33}(OH)_2.COOH + 2KBr$$

$$C_{17}H_{31}Br_4.COOH + \xrightarrow{4KOH} C_{17}H_{31}(OH)_4.COOH + 4KBr.$$

The acids so produced are called "hydroxyacids." A few are found occurring in nature, viz., dihydroxystearic, linoceric, etc. If instead of bromine HBr be added to an olefine acid, a monobrom derivative is produced, and this, on treatment with caustic potash as above described, passes into the monohydroxyacid.

$$C_{17}H_{33}.COOH + HBr \longrightarrow C_{17}H_{31}Br.COOH \xrightarrow{\downarrow KOH} C_{17}H_{34}OH.COOH$$

A monohydroxy acid containing one double bond is also known, viz., ricinoleic, $C_{17}H_{32}(OH).COOH$, which is found naturally occurring in castor oil.

The hydroxy derivative may be formed more readily by shaking the unsaturated acid with a warm alkaline solution of potassium permanganate. Two hydroxyl groups are formed at each double bond with the production of di, tetra, or hexa hydroxyacids, according as the original molecule contains one, two or three double bonds. Thus, by oxidation with alkaline $KMnO_4$,

Dihydroxystearic is obtained from oleic;
Tetrahydroxystearic (sativic) is obtained from linolic;
and Hexahydroxystearic (linusic) is obtained from linolenic.

It is important to notice that the more OH groups an acid contains, the more soluble in water it becomes; hexaoxystearic, for example, being fairly readily soluble in boiling water.

By treatment with hydriodic acid "addition" products are formed, which pass on further heating into corresponding

saturated acids. So, for example, oleic acid on treatment with *HI* at 200° C. passes into stearic.

The relationship to the saturated series is thus shown.

Under violent oxidation with concentrated nitric acid, the acids are broken at the double bond, giving rise to compounds of lower molecular weight.

All form salts with the metals. The lead salts of the higher acids are soluble in ether, while those of the saturated acids are practically insoluble. This affords a means of separating the unsaturated from the saturated acids.

Esters.—When an inorganic base like caustic soda is mixed with an acid, combination takes place and a salt is produced. Similarly the action of acids on alcohols gives rise to compounds called ethereal salts, or esters.

$$CH_3.COOH + NaOH \longrightarrow CH_3.COONa + HOH$$

Acetic acid — Sodium acetate.

$$CH_3.COOH + CH_3.CH_2.OH \longrightarrow CH_3.COOCH_2.CH_3 + HOH$$

Acetic acid — Ethylalcohol — Ethyl acetate.

The close analogy of the inorganic and organic reactions is seen from these equations, and it is to be noticed that in both cases water is formed as a by-product.

Processes like this, in which the reaction is accompanied by the formation of water, are called "condensation reactions," and this particular type of reaction is called "esterification."

If these esters are boiled with a large quantity of water, the reverse action takes place, *i.e*, the ester is converted into alcohol and free acid.

$$CH_3.COOC_2H_5 + HOH \longrightarrow CH_3.COOH + C_2H_5OH$$

This latter reaction is one of the most important in organic chemistry, and is known as "hydrolysis."

Now, suppose we start with pure alcohol and pure acid, and proceed to esterify. As the reaction proceeds, more and more water is formed. But this water tends to hydrolyse the ester formed, so a point will be reached, if the water is not removed, when the "hydrolytic action" is just equal to the "esterifying effect." At this stage the reaction will stop, and a mixture of

alcohol, free acid, ester and water is present. The addition of more water to the mixture results in the decomposition of some of the ester, and conversely the addition of more alcohol causes an increase in the amount of ester.

Such reactions, which attain a condition of equilibrium depending upon the relative proportions of reacting constituents, are called "reversible" reactions, and we will henceforward indicate them in equations by a double arrow, which serves to show that the reaction may proceed in either direction depending chiefly on the "relative mass" or concentration of the reacting bodies.

The above equation will then be written

$$CH_3.COOH + CH_3.CH_2OH \rightleftharpoons CH_3COOCH_2.CH_3 + HOH.$$

Accordingly, in the preparation of esters, some reagent must be employed to remove the water by combining with it immediately it is formed, and so permit of the esterification proceeding to more or less completion. The most common reagents for this purpose are sulphuric acid, dry hydrochloric acid gas and anhydrous zinc chloride.

By means of this process, many of the alcohols and fatty acids may be caused to combine to form esters. Those formed by the combination of the monohydric alcohols and fatty acids of low molecular weight are all volatile liquids, generally possessing a fruity smell and taste; while those produced by the esterification of the higher members are solid. The natural waxes consist of mixtures of esters of the higher fatty acids and alcohols.

Glycerides.—The polyhydric alcohols form esters in an exactly similar way. Those esters formed from the trihydric alcohol glycerol and the fatty acids are called glycerides.

$$\begin{array}{lll} CH_3.COOH & CH_2OH & CH_3.COOCH_2 + HOH \\ | & | & | \\ CH_3.COOH + CH\ OH & \rightleftharpoons & CH_3.COOCH + HOH \\ | & | & | \\ CH_3.COOH & CH_2OH & CH_3.COOCH_2 + HOH \end{array}$$

3 mols. of Acetic acid Glycerol Glyceride.

Since, however, glycerol possesses three hydroxyl groups, each of which may be replaced by an acid radicle, we get three kinds of glyceride, viz.:

Those in which only one *OH* group is replaced by an acid, and those in which two or three hydroxyls are substituted by acids.

The bodies so formed are called respectively mono- di- or tri-glycerides respectively.

As types, let us consider the esters formed by glycerol and acetic acid.

1 molecule of glycerol and 1 molecule of acetic acid give the monoglyceride

$$\begin{array}{l} CH_3.COOCH_2 \\ \quad\quad | \\ \quad\quad CHOH \\ \quad\quad | \\ \quad\quad CH_2OH \end{array}$$ monoacetin.

1 molecule of glycerol and 2 molecules of acetic acid give the diglyceride.

$$\begin{array}{l} CH_3.COO—CH_2 \\ \quad\quad\quad | \\ CH_3.COO—CH \\ \quad\quad\quad | \\ \quad\quad\quad CH_2OH \end{array}$$ diacetin.

1 molecule of glycerol and 3 molecules of acetic acid give the triglyceride.

$$\begin{array}{l} CH_3.COO—CH_2 \\ \quad\quad\quad | \\ CH_3.COO—CH \\ \quad\quad\quad | \\ CH_3.COO—CH_2 \end{array}$$ triacetin.

The three hydroxyl groups of glycerol may combine with the same acid or with two or three different acids. Thus we can have

$$\begin{array}{l} \quad\quad\quad\quad\quad CH_3.COO.CH_2 \\ \quad\quad\quad\quad\quad\quad\quad | \\ CH_3.(CH_2)_x COO.CH \\ \quad\quad\quad\quad\quad\quad\quad | \\ CH_3(CH_2)_x CH=CH.COO.CH_2 \end{array}$$

The former of these is called a *simple* glyceride, and the latter

two *mixed* glycerides. All these types are found in the fats and oils.

The pure individual glycerides of the higher saturated acids are crystalline solids of relatively low melting point. They are insoluble in water and are essentially fatty in all their properties. The lower members, like triacetin, may be readily prepared in the laboratory by the esterification process described above, but in the case of the glycerides of the higher fatty acids the preparation is difficult.

The naturally occurring animal and vegetable fats and oils consist essentially of mixtures of glycerides.

In the following table the formulæ and physical constants of a few of the more important glycerides which have been detected in natural fats and oils are given :—

TABLE SHOWING THE MORE IMPORTANT GLYCERIDES WHICH HAVE BEEN DETECTED IN NATURAL FATS AND OILS.

Name	Formula	Specific Gravity	Melting Point °C	Boiling Point °C	Occurrence.
Diglycerides—					
Dierucin	$(C_{21}H_{41}COO)_2.C_3H_5OH$	—	47	—	Old rape oil.
Simple Triglycerides—					
Tributyrin	$(C_3H_7.COO)_3.C_3H_5$	1·0324 at $\frac{20}{4}$	below −70	287 (760)	Butter fat.
Trilaurin	$(C_{11}H_{23}.COO)_3.C_3H_5$	·894 at $\frac{60}{4}$	45—46	—	Cocoanut oil.
Trimyristin	$(C_{13}H_{27}.COO)_3.C_3H_5$	·8848 at $\frac{60}{4}$	55—56	—	Muskat butter.
Tripalmitin	$(C_{15}H_{31}COO)_3C_3H_5$	·8657 at $\frac{80}{4}$	65	—	Palm oil.
Tristearin	$(C_{17}H_{35}.COO)_3.C_3H_5$	·8621 at $\frac{80}{4}$	71·5	—	Tallow and many fats and oils.
Triarachin	$(C_{19}H_{39}.COO)_3.C_3H_5$	—	—	—	Arachis oil.
Triolein	$(C_{17}H_{33}COO)_3C_3H_5$	·900 at $\frac{15}{4}$	−4	—	Most fats and oils.
Trierucin	$(C_{21}H_{41}COO)_3.C_3H_5$	—	31	—	Rape oil.
Triricinolein	$C_{17}H_{33}(OO)_3.C_3H_5$	·983 at $\frac{15}{4}$	4·5	—	Castor oil.
Mixed Triglycerides—					
Stearodipalmitin	$\left.\begin{matrix}(C_{15}H_{31}.COO)_2\\C_{17}H_{35}.COO\end{matrix}\right\rangle C_3H_5$	—	60	—	Tallow.
Palmitodistearin	$\left.\begin{matrix}(C_{17}H_{35}.COO)_2\\C_{15}H_{31}.COO\end{matrix}\right\rangle C_3H_5$	—	62·5—66·5	—	Tallow.
Oleodistearin	$\left.\begin{matrix}(C_{17}H_{35}.COO)_2\\C_{17}H_{33}.COO\end{matrix}\right\rangle C_3H_5$	—	44—45	—	Tallow.

DIRECTOR OF INDUSTRIES
Bengal

CHAPTER II

MINERAL OILS—PETROLEUM AND SHALE—MINERAL OIL REFINING.

The production and refining of the so called mineral oils constitutes one of the largest and most important branches of the oil industry. Long before the commencement of the Christian era the occurrence of oily exudescences on various parts of the earth's surface was known, and termed Rock Oil or Petroleum (Greek, *Petros-Oleum*). It was not, however, until the early part of the nineteenth century that any serious attempt was made to obtain the crude oil in quantity, and refine it into products of commercial value, and when one remembers that the world's output of petroleum during the year 1908 was over 27 million tons, it is clear that the progress made in this industry has been phenomenal. Just about the time when the exploitation of oil-bearing strata was attracting attention in America, James Young in England discovered and patented a process for obtaining "paraffine oil, or an oil containing paraffine, and paraffine wax, from bituminous coals." This process was afterwards extended to the preparation of oils and paraffin by the destructive distillation of shale, vast deposits of which had just been discovered in the lowlands of Scotland, and gave rise to the shale oil industry which has assumed great importance during the last quarter of a century. It is, therefore, from these two great sources that the mineral oils of commerce are obtained, viz., on the one hand from the simple distillation of naturally-occurring petroleum oil, and on the other hand the destructive distillation of shale.

Petroleum is widely distributed throughout the world, but the most productive districts are found in the United States of America, and in the neighbourhood of the Caucasus in Asia.

The crude oil is usually accompanied by gas and salt water and is apparently lodged in vast areas of pervious rock under

pressures as high as 600 lbs. to the square inch. The cause of such enormous pressure is probably due to either an accumulation of gas which, unable to escape, becomes compressed, or simply the hydrostatic pressure exerted by water at great distances from the oil gas area.

The origin of petroleum has engaged the attention of chemists for many years, and is still in a somewhat controversial state. In the opinion of some investigators, petroleum has an inorganic origin, while others ascribe an organic formation to it. Among the arguments deduced for the inorganic theory may be mentioned the formation of hydrocarbons by the action of water on carbides. Hydrocarbons in small quantity of a similar nature to petroleum have been obtained by treating carbides of iron and manganese (spiegeleisen) with dilute acids, and the formation of acetylene from calcium carbide is well known.

This experiment suggested to Mendeleef an hypothesis to account for the presence of petroleum. Mendeleef assumes that the interior of the earth is largely composed of iron, quantities of which are probably combined with carbon as carbides. Under the influence of water at high temperatures and pressures, hydrocarbons may have formed by interaction with these masses of iron, carbon and carbides.

Mendeleef advances many geological facts in support of the theory, such as the occurrence of petroleum in rocks of very different geological age, and the association of petroleum with volcanic activity. Recently Bekker supports this theory by the observation that the magnetic needle is affected in the neighbourhood of oil wells.

Further evidence in favour of the inorganic theory has lately been adduced by the experiments of Sabatier, Senderens and others. These workers have shown that acetylene may become reduced by hydrogen gas in the presence of minute amounts of finely divided metals (catalysts) to ethylene and even methane. The former may polymerise under certain conditions with the formation of petroleum-like oils.

The most satisfactory evidence on which an hypothesis of the formation of petroleum can be based would undoubtedly be the discovery of certain definite substances in the oil and its

associates whose origin was well known, such, for example, as inorganic matter, carbides, fossils, or certain organic products.

Such substances have recently been detected in crude oils and its distillates, and, as we shall see later, this fact gives strong support to the hypothesis of organic origin. In 1862 Sterry Hunt pointed out that petroliferous strata occasionally is found sandwiched between similar porous strata free from oil. He considers from this that oil must have formed by the transformation of organic matter in the strata in which it is met with. Many of the earlier authorities believed that coal or bituminous shale was the intermediate substance in the formation of oil from organic matter, but this theory has received but scant support from experiment.

Engler in 1888 was the first to alter the trend of discussion by an exceedingly interesting experiment. He distilled menhaden fish oil, triolein, etc., under a pressure of 10 atmospheres, and obtained a distillate of hydrocarbon oils, accompanied by gas, having all the properties of natural petroleum.

This experiment led Engler and others to ascribe the formation of petroleum to the destructive distillation of the fatty matter of animal remains, chiefly minute marine organisms. The conception has been elaborated by Engler and his collaborators in a magnificent series of researches, culminating in the discovery of the optical activity of petroleum. Distillates may be obtained from petroleum, which, when examined by the polarimeter, are found to rotate the beam of polarised light, some to the left, others to the right. Each portion has a definite maximum activity at boiling points, which are the same for different varieties of petroleum, and on continued distillation all the fractions of higher boiling point are dextro-rotatory.

Now the wax-like body cholesterol, which is an invariable constituent of animal fatty matter, yields on destructive distillation hydrocarbons which can be separated into *l* and *d* fractions.

These optically active distillates correspond in boiling point to those fractions isolated from petroleum mentioned above, and, like them, the active hydrocarbons of cholesterol all become dextro on continued distillation. Further, it has been shown that very small fractions of 1 per cent. of cholesterol derivatives would account for the optical activity of petroleum. Stronger

evidence for the theory of organic formation than this can scarcely be found. Engler recently summarises his view in the following terms: "The inorganic theories, though accounting for the production of hydrocarbons, fail to explain the optical activity which is undoubtedly due to decomposition products of cholesterol, as Marcusson suggested." The animal and vegetable matter was fermented when the more unstable nitrogen compounds broke up. Then saponification occurred, and finally a splitting up of CO_2 gave rise to hydrocarbons which cracked according to the equation

$$2C_nH_{2n+2} \longrightarrow C_{\frac{n}{2}}H_{\frac{2n}{2}} + C_{\frac{n}{2}}H_{2n+2}.$$

The methane homologues are stable, while the olefines polymerise to high molecular weight hydrocarbons and naphthenes.

Engler has suggested an explanation for the difference in composition of the American and Russian oils. On warming amylene with aluminium chloride for some hours a thick oil, similar to lubricating oil, and a light oil consisting chiefly of paraffin was formed, but no naphthenes. On the other hand, by heating amylene or lubricating oil under pressure, naphthenes and paraffins were formed.

He concludes, therefore, that since heating under pressure gives naphthenes, that the Russian oils which are rich in these compounds were formed under high temperature while the American product which contains little naphthenes were formed by long storage at relatively low temperatures. In this connection Gilpin and Cram found that on filtration of oil by capillary diffusion through fuller's-earth fractionation occurred, the portion passing through first being rich in paraffins, whilst the unsaturated compounds were left behind. Rakusin is of opinion that this has occurred in nature, since the paraffinoid oils are always found nearer the surface than the denser oils containing unsaturated compounds. He also observes that the paraffin content decreases with increase in geological age.

Crude petroleum varies widely in different regions, from a thin volatile liquid to thick tarry and even solid masses. The variations are to be ascribed partly to the geological arrangement of the district where it occurs, and also to the varying magnitude of

the physical forces of heat and pressure to which it has been subjected, and finally to its age. Much diversity of opinion has been expressed as to the mode of formation of the mass of solid hydrocarbons distributed over the earth, known as asphalt and bitumen. The simplest explanation of the way in which these products were formed is that of the evaporation of the lighter oils accompanied by oxidation, leaving a solid residuum. This is almost certainly true in the case of many of the big asphalt deposits, but on the other hand the mineral wax ozokerite possesses marked differences in composition to any residues obtained by distillation of petroleum in the laboratory.

Further, by the distillation of these solid bitumens light oils may be obtained, which gives force to the argument that bitumens may be the precursors of oils in certain cases.

The general appearance, specific gravity, etc., of petroleum from various parts of the earth is given in the table opposite.[1]

Petroleum, from whatever source, consists essentially of a mixture of hydrocarbons of various series together with a small percentage of nitrogenous basic matter, oxygenated bodies, and organic compounds with sulphur. Mabery recently summarised our knowledge on the composition of petroleum in these words: "Petroleum is a mixture in varying proportions, of a few series of hydrocarbons, the product from any one field differing from that of another only in the proportion of these series, and the number of the series."

On this view the oxygen-, nitrogen-, and sulphur-containing compounds, which are invariably present, must be looked upon, more or less, as impurities. A large number of homologues of the following series of hydrocarbons have been detected.

C_nH_{2n+2}	Paraffin
C_nH_{2n}	Olefine
C_nH_{2n}	Naphthene
C_nH_{2n-2}	Acetylene
C_nH_{2n-4}	Asphaltic (?)
C_nH_{2n-6}	Benzenes
C_nH_{2n-8}	Phenylethenes
C_nH_{2n-10}	Phenylethines
C_nH_{2n-12}	Naphthalenes

[1] See frontispiece for the distribution of petroleum over the earth.

TABLE SHOWING APPEARANCES, ETC., OF VARIOUS OILS.

	Locality.	Specific gravity.	Colour.	Observer.
American Petroleum	Washington	·771/·820	Yellow to dark brown	Redwood
	Bradford	·810/·819	Reddish	,,
	California	·827/·880	Dark brown to black	,,
	Canada	·858/·948	Brown to black	,,
	Mexico	·874/·970	Brown to black	,,
Russian	Balukhany	·873/·910	Brown to black	Redwood and Neuburger
	Baku	·886/·938	Brown to black	Neuburger and Noalhat
	Tiflis	·976	Brown to black	Redwood
Galician	—	·779/·898	Reddish-yellow to black	Neuburger and Noalhat
Roumanian	—	·845/·899	Dark brown	Redwood
Asiatic	Trans-Caspian	·912/·946	Black	Neuburger and Noalhat
	Persia	·773/1·016 (Daliki)	Black	Neuburger and Noalhat
	Burmah	·814/·877	Black and viscous	Neuburger and Noalhat
	China	·860/·881	Greenish	Neuburger and Noalhat
	Japan	·831/·882	Brown to greenish-black	Neuburger and Noalhat
	Borneo	·950/·953	Brown to greenish-black	—

Besides these there are probably present hydrocarbons of series containing much less carbon in the higher fractions and bitumens, the detection of which is well-nigh impossible, owing to the ease with which they are decomposed on attempting to separate them by distillation. The present state of our knowledge of the hydrocarbons constituting petroleum oil, is briefly stated in the following pages.

1. **Paraffin or Saturated Series.** C_nH_{2n+2}.—Representatives of this series are found in all oils examined. An almost complete series from methane CH_4 to triacontane $C_{30}H_{62}$ has been detected in Pennsylvanian oil. This series is found in the fraction of the oil boiling up to 380° C. Homologues of this series predominate in American crudes, but only relatively small quantities in Russian.

2. **Olefines.** C_nH_{2n}.— Members have been definitely detected in Canadian, Namer and Californian crudes, and indirect evidence of their presence in oils from other sources have been obtained.

In the process of distillation, however, olefines are formed by the decomposition of the paraffins, in accordance with the equation given above, for this reason it is difficult to state in all cases whether the olefine found in the distillate was present in the crude, or was formed from paraffins by partial decomposition.

3. **Acetylenes.** C_nH_{2n-2}.— Small quantities of acetylene gas were observed by Markownikow to be dissolved in Baku oil. Mabery isolated from Texas oil a number of homologues from C_3H_6 to $C_{12}H_{24}$, but is not sure that they are all true acetylenes; they probably contain a number of methylene rings united as in diphenyl.

4. **Naphthenes.** C_nH_{2n}.—These compounds, which are isomeric with the olefines, predominate in Russian oils, and are found in greater or lesser quantity in almost all crudes. A series from C_6H_{12} to $C_{19}H_{36}$ has been isolated.

5. **Series C_nH_{2n-4}.**—Compounds possessing this formula have been obtained from Texas crudes, but their structure is uncertain. It is possible that the hydrocarbons examined were not true chemical individuals, but mixtures of hydrocarbons containing olefine or acetylene linkages with those containing less hydrogen in the molecule than accords with the general formula of this group.

6. **Series C_nH_{2n-6}. Benzene Hydrocarbons.**—Benzol and its homologues have been isolated from all oils. Benzene itself occurs in Pennsylvanian, Galician, Baku, Tiflis, Rangoon and other crudes; xylene, isoxylene, cumene and pseudo-umene mesitylene and toluene in various oils,

7. **Series C_nH_{2n-8} and C_nH_{2n-10}.**—Compounds agreeing with these formulæ have been obtained from petroleum, but it is not certain that they are chemical individuals. They appear to be compounds containing unsaturated chains joined to benzene rings.

8. **Series C_nH_{2n-12}.**—Naphthalene $C_{10}H_8$ has been detected in Rangoon oil.

The principal method of investigation of the composition of the oils hitherto employed has been that of fractional distillation. This process consists in its simplest form of heating the oil in a retort, collecting the condensed vapours in portions, according to the temperature at which they are given off by the boiling liquid.

Since the compounds of high molecular weight suffer more or less decomposition at the temperature of the boiling point under atmospheric pressure, it is necessary to conduct the distillation under diminished pressure. Now the better the vacuum, the lower is the boiling point, and it has been observed that this particularly applies to the last few millimetres on the gauge. For example, a reduction in pressure of 10 millimetres of mercury, from 760 millimetres to 750 millimetres, reduces the boiling point of water from 100° C. to 99·6° C., a difference of only 0·4° C.; while a reduction in pressure of 10 millimetres, from 12 millimetres to 2 millimetres, brings the temperature of ebullition down from 14·5 to − 10° C., *i.e.*, a difference of 24·5° C.

This observation led Krafft, in 1906, to seek for a means of obtaining very high vacua, and resulted in his invention of the process of distillation in the vacuum of the cathode light—a method which has proved of inestimable value in the scientific investigation of oils and fats, mineral, animal and vegetable.

Briefly, the method depends upon the power of charcoal to absorb the last traces of air in a partial vacuum, when the charcoal is cooled by liquid air. Fig. 2 gives an idea of the apparatus.

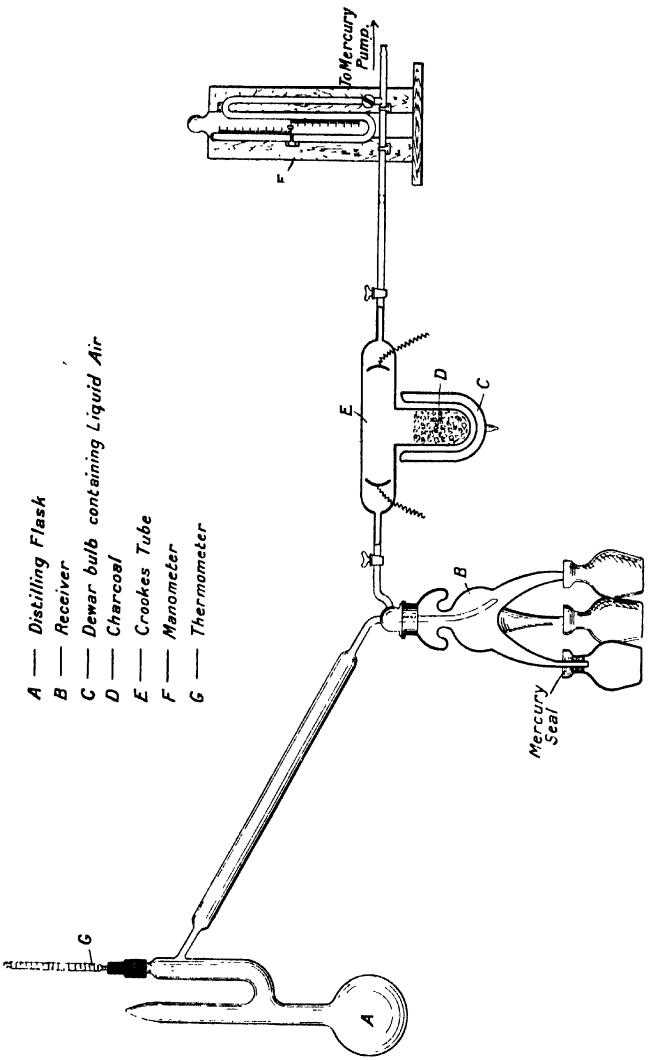


FIG. 2.—Apparatus for Distillation in the Vacuum of the Cathode Light.

The apparatus having been exhausted as far as possible by a mercury pump, the tube containing the charcoal is dipped in

liquid air, and so cooled to about −200° C. The trace of air left in the apparatus by the pump is absorbed by the charcoal, and a vacuum is produced which can no longer be measured by a mercury manometer. A Crooke's tube, which only begins to show striæ under the electric discharge when the vacuum is nearly perfect, is therefore used as a manometer. By means of this apparatus it has been possible to separate individual members of a whole series of homologous hydrocarbons, from $C_{15}H_{32}$ to $C_{30}H_{62}$.

Fractional distillation is a very useful means of separating the compounds of low boiling point from an oil, and by its aid our knowledge of the composition of the distillates boiling below 150° C. has been highly enriched. The method, however, has not proved very satisfactory for the isolation of hydrocarbons of higher boiling point. This is due partly to the difficulty of avoiding decomposition of the oil, which occurs to some slight extent even in the highest vacua, but principally to the tendency of the homologues to form constant boiling mixtures, *i.e.*, mixtures of hydrocarbons which behave as though they possessed a common vapour pressure.

Hence, while the composition of the lower boiling homologues of petroleum is fairly well known, the investigation of the higher boiling portion of the oil, residuum, etc., has, owing to the experimental difficulties, only recently been undertaken. Marcusson has pointed out that the fractions of petroleum of high boiling point chiefly consist of the following types of hydrocarbons:

1. **Unsaturated Hydrocarbons.**

(*a*) Cyclic or closed chains.

1. Aromatic, *i.e.*, benzene-like bodies.
2. Alicyclic, or terpene-like bodies.

(*b*) Aliphatic (olefines and polyolefines).

2. **Saturated Hydrocarbons.**

(*a*) Cyclic (polymethylenes, etc.).

(*b*) Aliphatic (paraffins).

The difficulty of separating these high molecular compounds is very great indeed, and it is only within the last few years that anything like satisfactory methods have been discovered.

Nastjukoff, in 1904, showed that ring compounds containing

a double bond when treated with formaldehyde and sulphuric acid form difficultly soluble substances, which he calls "formolites," whilst paraffin, naphthenes, and olefines are unaffected.

The weight of insoluble "formolite" which can be obtained from 100 cub. centimetres of oil is called the "formolite number," and is a measure of the amount of cyclic unsaturated hydrocarbons in the oil.

Nastjukoff found that in general American oils give higher formolite numbers than Russian.

The formolite reaction is carried out as follows:—27 cub. centimetres of oil are dissolved in 300 cub. centimetres of ligroin and 30 cub. centimetres of concentrated sulphuric acid added. The flask is cooled in ice and 15 cub. centimetres 40 per cent. formaldehyde added gradually, with continual shaking until no further development of heat occurs. The mixture is allowed to stand for one hour at room temperature, and then treated with 200 cub. centimetres of ice water. The acid liquid is then saturated with ammonia and the insoluble precipitate which forms separated off, washed with ligroin to remove all adhering unaffected oil, and finally with water to free it from ammonia. The precipitate is dried at 105° C. till constant. The weight of this precipitate per cent. is called the formolite number, and this multipled by 4/5 = percentage of cyclic unsaturated compounds.

The separated ligroin solution contains the olefines, alicyclic compounds, paraffins, and saturated naphthenes, which may be recovered by evaporating off the solvent.

The portion of the oil which is unacted upon by formaldehyde and sulphuric acid is found to possess lower specific gravity and higher viscosity than the original oil, from which it is clear that the unsaturated cyclic compounds possess relatively higher specific gravities and low viscosities. The above reaction does not, however, help to decide whether open-chain olefines are present.

It is known that the double bond in aliphatic unsaturated rings, and also in open-chain compounds, absorbs iodine.

Accordingly, experiments have been conducted on that portion of the oil which did not act with formaldehyde, in order to see whether it possessed the power of absorbing iodine. It was found that this fraction did absorb iodine, from which it is concluded

that olefine-like compounds are present in the oil. When these oils are treated with strong nitric acid, all the compounds which possess double bonds are attacked, while the saturated bodies remain unaffected.

In order to isolate these saturated compounds a portion of the oil was dissolved in ligroin, and shaken with nitric acid at -10° C. The unattacked solution of hydrocarbons was separated, washed with water, dried, and the solvent evaporated off, when an oil remained consisting entirely of saturated hydrocarbons. The results of these experiments on two typical lubricating oils are shown in the table on p. 44.

Summarising, Marcusson considers—

(1) The lubricating properties of the mineral oils are chiefly due to the presence of hydrocarbons which do not react with formaldehyde and sulphuric acid.

(2) That portion of the oil which combines with formaldehyde shows a higher specific gravity, and lower viscosity, than the original oil.

(3) American mineral lubricating oils, are in general richer in compounds which absorb iodine than Russian, *i.e.*, the American oils contain more alicyclic and olefine hydrocarbons than the Russian.

(4) The Russian oils contain more hydrocarbons which resist the action of nitric acid (*i.e.*, saturated compounds) than American.

It was stated on p. 36 that petroleum consists essentially of a mixture of hydrocarbons. There is, however, always present in the crude oils a small amount of foreign bodies containing sulphur, nitrogen, or oxygen, which, being considered as impurities, it is the object of the refiner to remove. These compounds may be grouped under three main classes:

(1) Nitrogen-containing compounds, generally of a basic nature.

(2) Oxygenated bodies, generally of an acid type.

(3) Sulphur compounds.

The nitrogen content of crude petroleum varies from 0·005 to 0·5 per cent. In Californian as much as 10 to 20 per cent. of the oil is composed of compounds of the type $C_{12}H_{17}N$. Six

Character of Oil.	Formolite precipitate, per cent.	Unsaturated cyclic hydrocarbons = ** per cent. Formolite number. A.	Fraction unattacked by H_2SO_4 and formaldehyde. Per cent. B.	Fraction unattacked by cold nitric acid. C.	Specific Gravity at 15° C.				Viscosity at 20° C.			
					Original oil.	A.	B.	C.	Original oil.	A.	B.	C.
1. American (refined)	28·9	25·7	71·3	73·0	·8910	·9069	·8856	·8807	11·0	4·2	14·9	9·0
2. Russian (refined)	14·9	11·9	88·1	75·5	·9011	·9196	·8986	·8932	14·1	—	21·8	14·1

members of this series were isolated by Mabery—namely, from $C_{12}H_{17}N$ to $C_{17}H_{21}N$—having boiling points ranging from 130 to 275° C. They all possess a nicotine-like odour and contain the tetrahydro quinoline nucleus.

Alkaloidal bases have been detected in Saxony and Galician crudes, and Peckham states that pyridine and quinoline derivatives of an alkaloidal nature are found in Californian oil combined with a feebly acid tar. Finally, nitrogen as salts of ammonium has been detected in the majority of crudes.

Oxygenated Substances.—A few tenths per cent. of oxygen is present in all crudes, combined in the form of "naphthenic acids." Much doubt still exists as to the true structure of these bodies, which appear to have been formed by the slow oxidation of the hydrocarbons.

The earlier investigators believed that their acid nature was due to the presence of a carboxyl group, but there is now much evidence in favour of an acid hydroxyl group, which would largely account for the weakly acid character manifested by some of these compounds. Charitschkoff is of opinion that these acids may be tautomeric, behaving sometimes as alcohols and sometimes as carboxylic acids thus—

$$R.CH_2.COOH \rightleftarrows R.CO.CH_2OH.$$

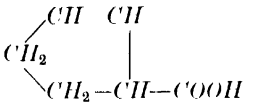
The naphthenic acids may be looked upon as derivatives of polymethylene acetic acids of the type $R . CH . COOH$, where R stands for a polymethylene or naphthene ring. On this view, for example, Markownikoff's octonaphthenic acid isolated from Caucasian oil would possess the formula

$$\begin{array}{l} CH_2.CH_2.CH.CH_3 \\ | \qquad\quad | \\ CH_2.CH_2-CH.COOH \end{array} \quad \text{or} \quad CH_2 \begin{array}{l} \diagup CH_2-CH_2-CH_2 \\ \qquad\qquad\qquad\quad | \\ \diagdown CH_2-CH_2-CH-COOH \end{array}$$

Hexa, hepta, nono, and deka naphthenic acids, all of which have been obtained from the alkali washings of the Baku refineries, would be formulated on a similar type. The compounds of low molecular weight are fairly strong acids possessing a characteristic odour. They are moderately soluble in water, and form salts with the metals; and since they are obtained in considerable

quantities from the refining of petroleum, more or less successful attempts have been made to use them in the manufacture of soap.

Derivatives of the unsaturated polyethenes are also known of the type



Sulphur Compounds.—Sulphuretted hydrogen is sometimes found dissolved in the crude, but the bulk of the sulphur found in the oil is present as organic sulphur compounds. Sulphur occurs to the extent of about 0·5 per cent. in many oils, as alkylsulphides, and Mabery and Quayle have isolated a series of thiothanes from Californian petroleum, of general formula $C_nH_{2n}S$, which they believe to be constructed on the type

These sulphur compounds are intensely difficult to remove, and impart to the oil an unpleasant raucous odour. The peculiar odour of Texas and Scotch oils is no doubt due in a great measure to the sulphur they contain.

Shale and Shale Oil.

While James Young was experimenting with his process for obtaining paraffin oil and wax by distilling bituminous coal at a low temperature, a bituminous mineral to which the name "shale" has been given was discovered in the Lowlands of Scotland.

Shale is a hard laminated rock varying from dark grey to black and containing from 15 to 30 per cent. of organic matter mixed with inorganic substances. When the shale is heated the organic matter suffers decomposition and distils off in vapours which when condensed yield a thick oil consisting essentially of a mixture of hydrocarbons not unlike some varieties of natural petroleum.

This hydrocarbon distillate is formed from the organic portion of the shale by the action of heat, and the process is known as "destructive distillation," because the distillates are different in

their chemical composition from the original substance in the still (distinction from simple distillation).

The organic matter of the shale has not been thoroughly isolated and examined, but it appears to consist of the fatty and albuminous products of decay of minute animal forms buried in mineral matter by a process of sedimentation in some earlier geological age. Artificial shales bearing a great resemblance to the natural product have been prepared in the laboratory by mixing diatoms and infusoria with clay and then baking the mixture until it becomes hard. Such artificial shales yield on destructive distillation oils very similar to that obtained from natural shale.

On an industrial scale the shale as it is received from the mines is broken into small pieces and thrown into a vertical retort heated by fire.

Various types of retorts have been devised from time to time, but it will suffice to describe briefly here the new Henderson retort. The upper portion of the retort is maintained at about 900° F. and the lower is heated to 1200 to 1300° F. The shale, enters by the hopper and the bulk of the oil is distilled from it in the upper chamber at 900° F. The "spent" shale, still containing some fixed carbon and nitrogen, then passes down the retort, where it is heated to 1200 or 1300° F. while at the same time superheated steam is passed over it. The products of distillation pass from the top of the retort through a pipe into the condensers. The object of the steam current is two-fold. In the first place it assists in carrying off the vapours and preventing too much decomposition of the oil, and secondly it acts upon the nitrogenous matter in the shale forming ammonia. Three products are obtained from the shale in this way:—

1. Crude oil.

2. Permanent gas used for heating retorts and lighting the works.

3. Ammoniacal liquor which is ultimately treated with H_2SO_4 for the preparation of sulphate of ammonia. The crude oil is dark green in colour and varies in specific gravity from ·860 to ·890. Owing to its high content of solid hydrocarbons it is semi-solid at ordinary temperatures, and the small percentages of

sulphur and nitrogen compounds impart a characteristic odour to it.

In chemical composition it resembles petroleum, in that it consists of a mixture of various homologues of the paraffin, olefine and naphthene series; but there the resemblance stops, since it contains much larger quantities of solid paraffins than any natural petroleum, a difference which can only be explained by comparing the modes of formation.

Whereas petroleum has been formed, at least in some cases, at moderate temperatures acting over long periods of time, shale oil is a product of rapid chemical decomposition at high temperatures. The latter reaction invariably results in the formation of crystalline paraffin from amorphous hydrocarbons accompanied by a deep-seated change in composition of the original bodies.

Mineral Oil Refining.

A small percentage of crude petroleum is nowadays employed as a fuel without any previous refinement, save that of allowing it to stand for a short time for the water to settle out, and a few of the wells in America yield viscous crudes which only require filtering and clarifying before being placed upon the market as natural lubricating oils. The vast majority of crudes are, however, subjected to a process of refining for the preparation of a series of products. The object of the refiner broadly is to separate the crude into fractions of different gravity and boiling point, and then to remove from each of these fractions all foreign matter of a non-hydrocarbon type.

The finished products, whether naphtha, kerosenes, or lubricating oils, should consist exclusively of hydrocarbons.

This object is attained by submitting the oil to fractional distillation, collecting the distillate in separate receivers according to the gravity or boiling point, and subsequently washing the distillates with mineral acid to remove basic matter, alkali to separate the impurities of an acid nature, and finally, in some cases, water to free the oil from all traces of the alkali.

This is the general principle utilised in any petroleum refinery, but the detailed method of conducting these operations and the

class of products manufactured varies widely from place to place according to the composition of the crude, the demands of the market, and the economic policy of the refiner. It is impossible here to describe in any detail the various modifications of refinery practice, which occupy a voluminous literature of a highly specialised character. A general description of the methods employed from the point of view of underlying principles will suffice.

We shall consider the operations under two headings:

1. Distillation.
2. Chemical and Physical treatment of the distillates.

Distillation.—A consideration of the composition of the crude oils will show that petroleum can be fractionated by distillation into any number of products boiling between different temperature ranges; and in fact the crude is frequently split up ultimately into a dozen or more fractions. This high degree of fractionation is, however, never conducted entirely at one works, the tendency of refiners being to specialise, one works simply separating crudes into volatile oils and residuum, while others concern themselves solely with the refractionation of naphthas, burning oils, or residuum, as the case may be. It is usual in the first distillation to split up the crude simply into four fractions, namely—

1. Crude naphthas, distilling up to about 150° C.
2. Crude burning oil distilling between 150 and 300° C.
3. Intermediate oil (wax distillate) above 300° C.
4. Residue.

The naphthas are purified by chemical means and redistilled, yielding light and heavy naphthas and a residue, which is put into the crude burning oil. Similarly, the burning oil fractions are purified and redistilled, yielding various grades of burning oils and a residue, put into the intermediate oil. In some cases the residuum requires only physical treatment before being placed upon the market as a lubricant, but more generally it is transferred to another retort and distilled in a current of superheated steam until dry.

The distillates are washed and redistilled in steam, sometimes assisted by a vacuum, the various grades of cylinder oils being thus obtained.

Distillation of the Crude.

The crude oil is distilled from large cylindrical stills by direct fire, and the fraction which comes over below about 150° C. is collected and set aside for further treatment. The distillation is continued sometimes with the aid of a "little" superheated steam, and up to 250° C. or 300° C. the crude burning oil distillate is collected; as the temperature rises, more or less decomposition of the high molecular weight hydrocarbons occurs, and the distillate consists of heavy burning oil, lubricating oil and paraffin wax, sometimes called "cracked distillate," because the the decomposition is accompanied by a cracking noise.

It has been mentioned before that the open chain hydrocarbons containing over 20 carbon atoms do not boil at ordinary pressures undecomposed, although it is possible to distil them unchanged by passing large quantities of superheated steam into the retort. The mechanism of this decomposition process is not perfectly clear, but it certainly results in the formation of more olefines and paraffins of lower molecular weight, and even permanent gas, and may proceed according to the following series of equations:

$$C_{20}H_{42} \longrightarrow C_{10}H_{20} + C_{10}H_{22}$$

Paraffin — Olefine — Paraffin

$$(C_{10}H_{20})_x \qquad C_5H_{10} + C_5H_{12}$$

$$(C_5H_{10})_x \qquad CH_4 + C_4H_8, \text{ etc.}$$

It is, however, very important to note that as a result of this "cracking," the percentage of paraffin wax which may be obtained from the crude is very materially increased, a phenomenon which may be due not entirely to decomposition of the hydrocarbons in the strict chemical sense, but also to alteration in the physical state of the hydrocarbons which constitute wax.

These particular hydrocarbons are present in the crude oil in an amorphous state, probably as a colloidal suspension, and the

effect of heating the oil to high temperatures undoubtedly results in a transformation to a crystalline form no longer colloidally suspended, and hence capable of easy removal by pressing. At the same time dry heating for too long at a high temperature results in excessive decomposition, and although the yield of illuminating oil may be thereby increased, it is at the expense of the wax and lubricating oil fractions. The art of the refiner at this stage, therefore, lies in carrying out the distillation at the proper temperature and speed, by admitting more or less superheated steam to the still to moderate the cracking, with the object of carrying over the whole of the wax hydrocarbons in the neutral or intermediate fraction, since, if any be left in the burning oils, it impairs their illuminating power while its presence in the residuum intended for cylinder oil stock seriously affects the cold test and viscosity.

Distillation of the Fractions.—Each fraction obtained from the crude, as described above, is subjected to chemical purification processes to be described in the following pages, and then refractionated to obtain more homogeneous products, *i.e.*, products of fairly narrow boiling point limits.

The naphtha fraction is usually distilled from retorts heated by steam coils, and separated into light and heavy naphtha, each of which products may, if desired, be further divided into gasolines or motor spirit, stove gasoline, solvent naphtha, etc.

The residue remaining in the naphtha stills, known as heavy ends, is put into the crude burning oil fraction, which is likewise redistilled, after treatment, for the production of various grades of illuminating oils, the lighter distillates from this operation constituting the commercial kerosines, while the heavier portions are known as water-white oils, and are excellent illuminants.

The "neutral"[1] fraction which, as we have seen, comes over after the burning oils, is not usually chemically treated right away, but distilled once more with a small quantity of superheated steam to induce further cracking and render the paraffin wax more crystalline, after which it is cooled below the solidifying point and pressed in hydraulic presses to remove the paraffin

[1] So called because it usually is fairly free from impurities of a non-hydrocarbon type.

scale which it contains. The filtrate from the presses, known as "pressed distillate," may or may not require chemical treatment, according to the quality of the crude and the care taken in distilling. In any case the pressed distillate is again returned to the still and "reduced" by a current of superheated steam. The steam removes the lighter portion which, after clarifying and filtering, is sold as spindle or light machinery oil. The residue or reduced pressed distillate is then clarified, filtered, etc., and placed upon the market as viscous neutral, or heavy machinery oil.

The residuum left in the crude oil still constitutes cylinder oil stock, and the method employed to prepare heavy steam cylinder oils from it varies according to its composition.

In some cases superheated steam is led into the retort which is then heated by fire and distilled to dryness, leaving a residue of pitch. In other cases all that is necessary is to blow open steam through the oil to remove traces of volatile matter, then clarify and filter through various depths of charcoal or earth, when a greenish coloured viscous cylinder oil known as "Pale filtered cylinder oil" is obtained.

Some crudes yield only a small percentage of poor quality cylinder oil, and in these cases it rarely pays to attempt the preparation of lubricants from it. In this case the residuum is sold as fuel oil for use in steam raising and internal combustion engines.

During the distillation large quantities of permanent gas, chiefly methane, are formed from decomposition processes, and this serves admirably as fuel for the boilers and stills of the refinery.

One other recent development of the petroleum industry must be mentioned. Natural gas, which invariably accompanies crude oil, and consists essentially of mixtures of methane, ethane and propane, carries with it small quantities of the higher members, butane, pentane, hexane, etc.

These highly valuable liquid hydrocarbons may be extracted from the gas by compressing, refrigerating or bubbling it through heavier fractions, and this process is now commercially carried out, and affords a good supply of volatile matter for incorporation with the lightest fractions from the stills for motor spirit.

Each of the distillates from petroleum, before being placed upon the market is, as above mentioned, treated with acid and alkali respectively. The most general acid employed is concentrated sulphuric of 66 B. (1·76 sp. gr.). In some cases sulphuric anhydride is added to the sulphuric acid, when a more energetic action is required. Patents have been taken out for the utilisation of acetic acid, liquid SO_2, etc.

About 4 ozs. of the acid is used for every gallon of oil to be treated, and the mixture is violently agitated, air being blown through the liquid in lead-lined tanks. After about 30 to 40 minutes agitation the mixture is allowed to stand until complete separation of the acid occurs, when the acid layer is run off into a separate tank, and is known as "acid tar."

The oil is then pumped into another vat where it meets a solution of caustic soda. The concentration of the caustic varies somewhat with the nature of the oil to be refined, previous tests being necessary on small samples, to ascertain the concentration which is least likely to form troublesome emulsions when agitated with the oil. In some cases the oil is distilled over concentrated caustic lyes, but in general after violently mixing the oil with 1 to 2 per cent. of the soda solution, the separated lyes are withdrawn, and the oil is either warmed, allowed to stand to clarify, or washed with water to remove traces of the alkali. The caustic lyes obtained from the washing are known as "soda tars."

The reactions which take place between the oil and sulphuric acid are somewhat obscure. Tumsky, quoted by Redwood, writes: "The petroleum loses and the acid gains in volume to an extent often amounting to 5 to 8 per cent. of the petroleum. The tar products dissolve and impart a deep brown colour to the acid while the aromatic hydrocarbons, and many of the other unsaturated hydrocarbons are converted into sulpho-acids. The acid is specially instrumental in removing the oxygen-containing bodies; in fact, by continuing the treatment, the petroleum can be completely deprived of oxygen. On subsequently diluting the acid, an emulsion is formed, the surface of which is covered with an oily liquid having an odour somewhat resembling that of oil of turpentine or camphor. The action of the sulphuric acid is

more complicated than appears at first sight, for sulphurous acid is evolved in some quantity, and this is not accounted for by the actions referred to. Reduction of the acid evidently occurs, but the reducing agent is not as yet known. Even when the acid treatment is repeated as often as ten times, colour is still imparted to the acid, and further evolution of sulphurous acid occurs. It has been suggested that the acid has also an oxidising action, and this view is partly supported by the increased action when the treatment is assisted by heat, and by the greater refining power of Nordhausen sulphuric acid as compared with the ordinary acid." More recently the theory of surface action or colloid chemistry has been invoked to explain the action of the acid. Without entering into details here, it may be mentioned that when certain substances of high molecular weight are treated with solvents under certain conditions, a solution is produced which, although perfectly clear to the eye and presenting in every way the general appearance of a true solution, yet behaves in many ways differently to solutions of crystalloids, *e.g.*, salt in water, etc. A good example is afforded by albumen and water. Such solutions possess little or no osmotic pressure, and when examined by the ultramicroscope are found to consist of exceedingly minute particles of albumen distributed throughout the water. These "solutions" have been termed "pseudosolutions" or "colloidal suspensions." Their most characteristic properties may be summarised thus:

(1) They are optically heterogeneous, *i.e.*, when viewed by a microscope placed at right angles to a parallel beam of light passed through the solution in a quartz cell, shining particles in rapid motion are seen, to which the name "microns" has been given. (Principle of the Ultramicroscope.)

(2) When treated by certain chemical reagents or subjected to physical forces, such as heat, light, and electricity, the "solution" is destroyed, and the suspended matter thrown down, *e.g.*, a colloidal suspension of egg-albumen in water is "coagulated" by heat, currents of electricity, mineral and acetic acids, and certain metallic salts.

Now petroleum has been found to be optically heterogeneous, and it is thought by many that the resinous and asphaltic bodies of high molecular weight, which are always present in the crude, are not really "dissolved" in the oil as a true solution, but exist in colloidal suspension. Schültz[1] considers that the action of sulphuric acid is "colloidal," resulting in the coagulation of the resinous pitches and asphaltic substances in the oil. On this view, "the unrefined oil is an "oleosol" of high molecular weight condensation products. By the treatment with concentrated sulphuric acids these colloid bodies become partly separated, and an "acidsol" forms in the acid layer."

This view receives support from the fact that the colour may be discharged, and the oil freed from asphaltic matter by simple filtration through charcoal or earth, certainly a physical or surface action. Nevertheless, as Gurwitsch points out, quantities of sulphonated organic compounds are always found in the acid tar, which suffices to show that "the chemical process plays a very great role." These observations of Schultz, Rakusin, and others are of very great interest in directing the attention of investigators to the colloid aspects of petroleum, and indeed of all oils.

In the author's opinion these views are destined to play a great part in the future study of oil and its purification.

We shall have occasion to discuss this further later on.

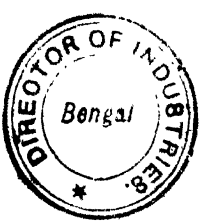
The action of the soda is of course clear. The oil, after washing with sulphuric acid, contains, in addition to the naturally-occurring acid matters, sulphonated acids, etc., which dissolve in the alkaline solutions, and so are removed.

The number of washings necessary to produce a pure oil obviously depends on the quantity and nature of the impurities in the crude distillate.

The bulk of such impurities are originally present in the crude, but the method of distillation is in part responsible for them.

Accordingly the operations of distilling and refining are more or less intimately related, and it may be taken as a general rule that the more care taken in the distillation the less refining is necessary.

[1] Pets. 5, 205 and 446.



Distillates from the best American crudes rarely require more than one treatment with acid and soda respectively, but in the case of the sulphurous Texas oils, as also shale oil, two or more treatments are required to produce an oil of first-class quality.

The composition and analytical constants of petroleum products vary so widely with differences in origin that it is only possible to indicate broadly their more important features.

Motor spirit or light benzine varies in gravity from ·650 to ·720 and distils completely between 30 and 120° C. to 140° C.

It is valued by the distillation test, gravity and calorific power. Chemically it should be quite free from acids and alkalies, and consist essentially of saturated hydrocarbons, paraffins and naphthenes up to 6 or 7 carbon atoms.

Solvent naphthas, used in the extraction of oils and the manufacture of paint and varnish thinners, range in gravity from ·700 to ·740.

The product of the petroleum refinery is usually again fractionated by spirit distillers to prepare grades of different flash point and volatility.

Illuminating Oils possess gravities from ·800 to ·825, the better qualities being usually at ·790. In general, a high gravity oil is a better illuminant than a low, within certain limits.

The oils should be light coloured to water-white, free from all inorganic matter and acids.

The minimum flash point is fixed by law in civilised countries, the English limit being 73° F. Abel.

The presence of wax in the oil spoils its illuminating power, and causes it to solidify or cloud at comparatively high temperatures, *i.e.*, 40° F. The high flash distillate known as water-white oils of about ·800 gravity are excellent burning oils.

The non-viscous neutrals or spindle oils of Pennsylvanian origin range from ·850 to ·870, while the viscous neutral (machinery oils) fall between ·880 and ·920. As they issue from the press they are usually red coloured, but may be bleached by filtration or exposure to sunlight to a pale lemon yellow.

The flashing temperature, generally over 350° F., and viscosity constitute important constants in their technical analysis.

The viscous steam cylinder oils also vary greatly in their

specific gravities according to their origin, viz., from ·885 to ·920. By filtration the gravity is slightly reduced.

"Vaseline" is a product, the preparation of which is more or less secret; it may, however, be prepared by carefully distilling certain residua in vacuo and filtering the distillate through char at temperatures only slightly above the melting point.

The yields from Pennsylvanian and Russian petroleums are on the average as follows:—

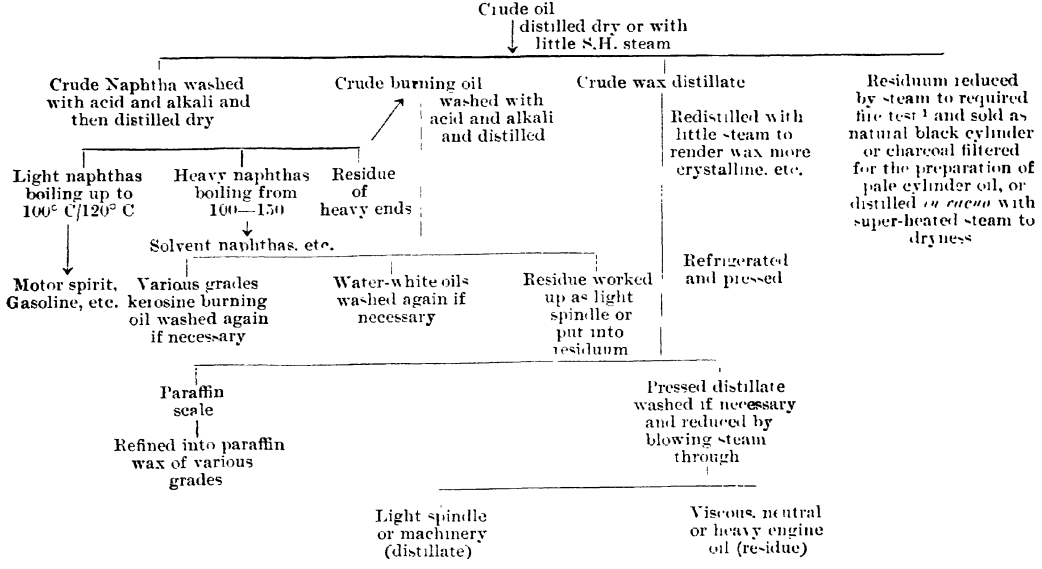
	American.	Russian.
Gasoline . .	1·0 to 3·0 per cent.	5 to 10 per cent.
Naphthas . .	12 to 15 per cent.	
Illuminating Oil .	50 to 55 per cent.	30 to 40 per cent.
Lubricating Oil .	16 to 18 per cent.	40 to 50 per cent.
Paraffin Wax . .	2 to 25 per cent.	nil.
Pitch . . .	—	nil.
Residuum . .	—	10 to 15 per cent.
Loss . . .	8 to 10 per cent.	—

Crude shale oil is refined by a series of operations very similar to those described for petroleum, except that rather more cracking is allowed during the distillations. The first operation consists in heating the crude in fire-heated stills with a small quantity of super-heated steam to complete dryness, whereby the oil is still further decomposed and a somewhat thinner distillate obtained, together with quantities of gas which is used for heating and lighting in the refinery.

The distillate is known as "once-run oil," and the still residue is coke. The once-run oil is treated with acid and alkali, and again distilled into three fractions, known as crude naphtha, twice-run oil, and a highly fluorescent product called green oil. Considerable cracking occurs again in this distillation, coke and gas being formed in fair quantity.

The crude naphtha is then chemically treated by acid and alkali, and distilled in steam-heated retorts, yielding a distillate of refined naphtha (·720–·760 gravity), and a residue of heavy oil which is put into the twice-run fraction.

DIAGRAM SHOWING THE GENERAL SCHEME OF PETROLEUM DISTILLATION.



[1] The distillation of cylinder stock in the refinery is usually controlled by determining the flash and firing point (fire test) of samples from time to time.

The twice-run oil on washing and redistilling yields various grades of illuminating oil from ·800—·820 gravity, which usually require some further treatment with acid and soda before being placed on the market.

It should be noted here that in general the distillates from crude shale oil require far more chemical treatment than petroleum products before an oil of equal purity is obtained. This is due not only to the difference in composition of the crudes, but to the greater decomposition induced in the distillation of shale oil resulting in the production of various impurities of a resinous nature, as a result of which the loss on refining is comparatively great, a disadvantage which can be to some extent minimised by careful attention to the method of distillation.

The green oil consists of a mixture of crude lubricating oil and paraffin wax.

It is slowly cooled[1] to about 5° F. and placed in the filter press. The oil which runs out shows a deeper fluorescence, and is known as blue oil, while hard scale, melting from 105—115° F., remains in the press, and is removed to the wax refinery. The blue oil after chemical treatment is fractioned by superheated steam distillation into—

1. Gas oil, from which, by subsequent distillation, a heavy burning oil or mineral colza may, if desired, be obtained.
2. Light oil, which on washing, gives ·865—·875 gravity, machinery or spindle oil.
3. Heavy oil containing a little paraffin wax, from which, by cooling and pressing, soft scale and ·885 machinery oil respectively is obtained.

Paraffin Wax.—The paraffin scale obtained by pressing green oil consists essentially of a mixture of homologues of the saturated hydrocarbon series of various melting points, and in order to obtain a hard wax it is necessary to remove all the bodies of low melting point. This is attained by the process known as "sweating."

The scale is melted and allowed to stand at about 180° C. for a short time to clarify, and then run into moulds to solidify. The solid blocks (about 2 feet × 1 foot × 6 inches) are placed on

[1] Rapid chilling must be avoided, otherwise the paraffin crystals are too small.

inclined trays and exposed to a temperature 20° or 30° F. below the melting point of the final product intended to be obtained, whereby the hydrocarbons of low melting point are liquified and ooze out, leaving a " cracked " cake of solid wax.

The drippings are collected, cooled, and subjected to a similar process at a somewhat lower temperature to obtain wax of inferior melting point.

This system of successive cooling and sweating is usually carried out in four stages yielding respectively waxes melting at 120° F. (25 to 30 per cent.), 115° F. (40 per cent.), 110° F. (20 per cent.), 100° F. (10 per cent.), and a small quantity of oily matter which is put into the blue oil fraction.

The various grades of wax are subsequently melted, churned up with charcoal to bleach, and finally clarified and cast into blocks.

The total yield of wax of all grades from crude shale oil amounts to 12 to 15 per cent., from American petroleum 1 to 5 per cent., and Galician 8 to 10 per cent., while Russian crudes yield none.

Paraffin wax is valued according to its melting point, colour, and odour. The best qualities are translucent whitish products free from odour and tasteless. It finds great application for a variety of purposes, notably in the manufacture of candles, polishes, waterproofing, and insulating materials.

CHAPTER III

NATURAL SOURCES AND METHODS OF PREPARATION OF THE SAPONIFIABLE OILS AND FATS

Natural Sources of the Saponifiable Oils and Fats.

Fatty matter is found as an essential constituent in all forms of vegetable and animal life, where it serves as a reserve supply of nourishment for the growing tissue. The fat is generally present in the form of fine globules suspended in the cell fluids, but occasionally it is found in the vegetable kingdom as crystalline needles. In the plant the most abundant supply of oil is found either in the seeds or the fruit, where it is always associated with other reserve products, chief of which are proteins and starch. Chlorophyl and other colouring matters are also present, particularly in the fruit. The process by which oil is formed in the organism is not quite clear, but it is highly probable that it is formed both by the decomposition of protein and from the carbohydrates, cellulose, sugar, etc. The latter view receives support from the observed fact that during the ripening period of a plant the oil content increases, while the starch diminishes. How far climatic conditions, temperature, etc., influence the nature and quantity of oil in the plant has not yet been sufficiently studied to enable any very definite conclusions to be drawn, beyond the fact that warmth appears to favour a high oil content; hence the remarkable quantities of oil obtainable from most tropical plants.

The number of plants from which oil has been obtained and examined is legion, but up to the present comparatively few find any extensive application in the oil industry. There can be no doubt, however, that in the near future the progress of scientific methods of cultivation and increased transport facilities in the tropics will bring into the market vast quantities of hitherto but little known oils.

The fat obtained from all land animals is solid at ordinary temperatures, but during life is present in a liquid state. Liquid oils are only found in the cold-blooded animals (fish, etc.).

The fine globules of fat are surrounded by a membrane of protein and form a network of cellular tissue (intercellular fats). Considerable quantities are present also between the muscles and cells of the various organs (intracellular fat).

The blood, lymph, bone marrow, and secretions of the animal body also contain small quantities of fat. The fat of very young animals contains somewhat less olein than that of a fully matured animal, and, further, the composition of the oil varies with the nature of the foodstuffs. Phosphorised fats (lecithin and other phosphatides) are found in all animals. Fatty matter is undoubtedly synthesised in the animal body chiefly from the carbohydrates of the foodstuffs, a fact which is utilised in the feeding of live stock. The chief animal fats and oils which find industrial application are:

Tallow, from mutton and beef;

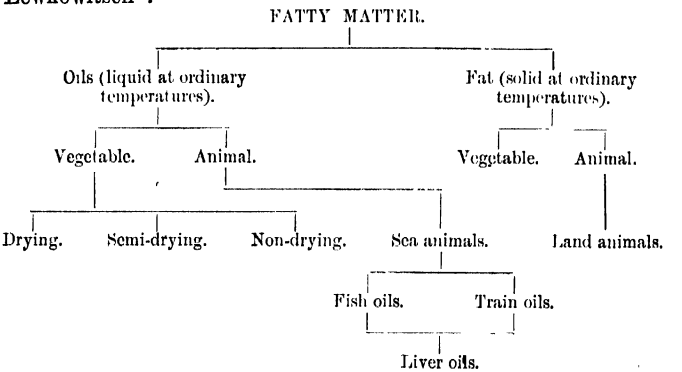
Lard, from the intracellular fat of the hog;

Bone fat, from the marrow of bones;

Horse fat;

Fish oil, chief of which are (*a*) liver oils; (*b*) blubber from the whale.

The following scheme of classification has been suggested by Lewkowitsch[1]:



[1] Lewkowitsch: Oil, Fats and Waxes.

All the vegetable oils contain phytostearol and no cholesterol, while all the animal oils contain cholesterol and no phytostearol.

The presence of one of these substances therefore decides whether an oil is of animal or vegetable origin.

The animal oils and fats are nowadays obtained as by-products of the great slaughter-houses and canning factories from the carcases of hogs, oxen, sheep, goats, and horses.

The fish oil industry is also of great importance, and comprises the extraction of the fatty matter from whales and a variety of fish.

The more important commercial vegetable oils and their botanical sources are indicated in the table below (Ubbelohde):

Oil.	Order.	Genus and species.	Number of grammes of oil per 100 grammes of seed.
Palm . .	Palmaceae	Elaeis guineensis Jacq.,	62/72 (fruit)
Coco-nut oil	,,	Cocus nucifera, L.	40/45 (copra)
Hemp seed	Moraceae	Cannabis sativa, L.	25/35
Poppy seed	Papaveraceae	Papaver somniferum, L.	41/50
Rape . .	Cruciferae	Brassica Napas, L.	35/40
Earth nut . (Arachis)	Leguminosae	Arachis hypogaea, L.	45/50
Soya bean .	,,	Glycine hispida	15/23
Linseed .	Linaceae	Linum usitatissimum, L.	32/41
Castor .	Euphorbiaceae	Riconus communis, L.	46/53
Croton .	,,	Croton Tiglium, L.	53/60
Cotton seed	Malvaceae	Gossypium herbaceum, L.	24/26
Shea butter	Sapotaceae	Butyrospermum Parkii	27/52
Olive . .	Oleaceae	Olea europaea, L.	40/60 (fruit)
Sesamé .	Pedaliaceae	Sesamum indicum, L.	50/58
Sunflower .	Compositae	Helianthus annuus, L.	21/22

Commercial Preparation of the Fats and Oils.

The fats and oils are obtained from the raw materials by three distinct processes:

1. By melting out or "rendering."
2. By pressing out, or "expression."
3. By extraction with solvents.

The first of these processes is confined almost entirely to-day to the preparation of fats from animal tissue, but in West Africa and uncivilised countries, considerable quantities of oil are, however, obtained from seeds by a melting-out process, still practised by the natives.

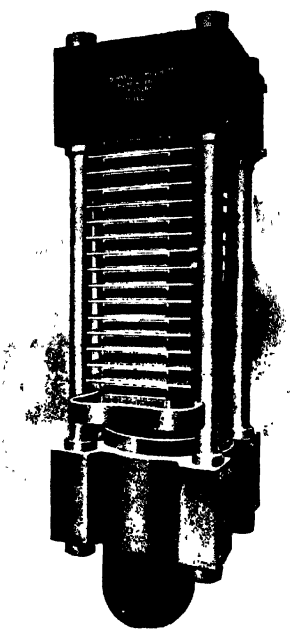


FIG. 3.—Oil Press. (By permission of Messrs. Rose, Downs & Thompson.)

The expression process is largely used in the treatment of the seeds and fruits of plants. This process was practised at least two thousand years ago, and was one of the earliest methods of preparing fats, but the modern expression process may be said to date from the discovery, in 1795, by Joseph Bramah, of the hydraulic press, and by far the largest quantities of fatty matter are nowadays prepared by this process. The extraction of oils by means of solvents is of comparatively recent date, and was originally applied to the preparation of oil from by-products of certain industries, such as wool-scouring, leather-dressing, and sewage. During the last few years, however, great advances have been made in the preparation on an industrial scale of high-class solvents, and so the extraction process now finds a wide and growing application.

In many works only one of these three processes is employed, but in some cases two or more methods are used conjointly. The choice of either of these processes for the extraction of an oil depends upon several factors, chief of which are the use to which the product is to be applied, and the relative value of oil and the residues.

Extraction of Oil from Animal Tissue.—The raw material for extraction is of a very varied nature, depending not only upon the type of tissue employed, but also upon its age and previous history. Animal tissue is particularly prone to decomposition when insufficient attention is devoted to the method of storage, and tissue which has been allowed to stand until decomposition is far advanced is enormously reduced in value as raw material for the oil industry. This is due to two causes. On the one hand, the combined influence of bacterial and enzymic action on the protein matter of the tissue results in the formation of large quantities of evil-smelling and highly objectionable soluble decomposition products, which are removed together with the oil, to which they impart pungent odours and unpleasant taste. The removal of these decomposition products from the extracted oil by refining is difficult and costly. On the other hand, fatty matter in the presence of decomposing protein suffers hydrolytic decomposition, with the result that the oil possesses a high content of free fatty acids and is very dark in colour. The exact nature of the changes which animal tissue undergoes during decomposition is unknown. It is certain, however, that bacteria play a great part in the reaction, and consequently in order to obtain a product possessing the minimum of decomposition it is necessary to store the tissue at low temperatures, since at the freezing point of water and below, bacterial activity is reduced to a minimum.

Washing and Preparation of the Tissue for Extraction.—The crude, raw material, before being placed in the extractor, requires to be thoroughly washed with water and then broken up. This is usually accomplished by passing the tissue through cylindrical wire machines rotating in a trough of cold water. The clean product is then dried, disintegrated into small pieces and placed in the extractor.

Extraction.—The rendering is carried out by either open fire, steam, or hot water. In the latter case the water may be rendered acid or alkaline previous to use. Various modifications, mainly of a mechanical nature, of extracting apparatus are employed, but the principle remains the same throughout: the fat-containing cell swells and bursts under the influence of the heat, setting free the oily contents, which flow down into a receiver placed below.

In order to accelerate this bursting of the cell wall, patents have been taken out for the addition of from 5 to 10 per cent. of concentrated sulphuric acid to the water in a water-extraction process. The acid attacks the membrane, which accordingly readily bursts, permitting the extraction process to proceed more rapidly. The use of alkaline water, intended to abstract the free fatty acids, has now been practically given up, since the formation of persistent emulsions renders the process slow and inefficient.

In the dry process, considerable quantities of pungent vapours are evolved, formed by the decomposition of the glycerides and tissue under the influence of heat. To avoid contamination of the atmosphere with these vapours, it is usual to arrange a system of flues by means of which the volatile matter is passed into the furnace and burned.

A process for carrying out the rendering in a vacuum has been patented, in which it is claimed that all traces of readily volatile impurities are removed during the extraction, all objectionable smell is avoided, and the product obtained possesses a high degree of purity.

Sometimes the raw fat is placed in the digestor, and treated with steam, or heated by fire, to moderately high temperatures, in order to obtain, as complete a rendering as possible in one operation. This, however, tends to decompose the oil, and yields a product of comparatively poor quality. For the preparation of pure fats of good quality, intended for edible or other purposes, care must be taken to secure the raw material fresh from the carcase of the animal and to render it in the first case at as low a temperature as possible. The residue from the first digestor still contains some fat, which is extracted either by subjecting

it to a higher temperature, or the action of superheated steam sometimes under pressure in autoclaves.

This causes a considerable amount of hydrolysis of the fat and tissue to occur, hence the product obtained is much inferior in quality to that of the first extraction. In some works the fat is extracted from the residue of the rendering by expressing it under hydraulic pressure. This, again, leaves a residue containing a small percentage of fat which may be removed by extraction with solvents. The fully extracted tissue, consisting simply of fibre and cell protein, is fit only for manure, but the residue from the presses or digestors, if not further treated with solvents, is sold as a food-stuff. Bone fat is sometimes obtained by a rendering process. Some manufacturers extract the fat by boiling the bones in a vat with water, and skimming off the fatty layer, which rises to the surface. In other cases the bones are treated with direct steam in a specially constructed digestor, when the fat melts out and is run off at the bottom of the vessel. More frequently, however, the preparation of fat from bones is accomplished by extraction with solvents.

The Preparation of Fats and Oils by Expression.

This method of preparation of oils is of predominant importance, and is nowadays almost universally employed, for the production of vegetable oils. Two methods of operation are in use in this country, known respectively as the English and the Anglo-American systems. Broadly, four distinct operations are necessary:—

1. Purification of the seeds.
2. Crushing the seeds to a pulp or meal.
3. Heating the meal.
4. Expression of the oil from the crushed seed, by hydraulic pressure.

The seed as received by the crusher is mixed with sand, dirt, and occasionally small quantities of different kinds of seeds from that which it is intended to obtain the oil; the seeds are therefore first passed through cleaning machines, which remove dirt and foreign bodies, and finally into ingeniously contrived cylindrical wire machines, which effect a more or less efficient

sorting of the individual seed. The clean seed is then decorticated, if necessary, placed in a mill, and ground to a meal. The meal is mixed with a little water and warmed in steam-jacketed kettles, before being filled into the bags for pressing. The object of the heating is to render the oil more fluid, and so easier to express, and also to assist in coagulating the albuminous matter of the meal. On the correct heating of the meal, the quantity and quality of the oil obtained largely depends, since with too high a temperature the colour stuffs and flavouring principals are dissolved by the oil to an excessive degree and the expression of oils intended for edible purposes is for this reason generally carried out in the cold. It is usual to press the cake, first with moderate pressure, when oil of the best quality is obtained (first pressure oil); the pressure is then increased and a further yield of oil results (second pressure oil).

Finally, the meal may be ground up again, further heated, and once more pressed. It is not the object of this book to describe the machinery employed in these operations, and for a discussion of the merits and details of various types of mills and presses the reader is referred to the standard engineering treatises on the subject.

The quantity of oil left behind in the cake depends upon a number of important details, such as the method of the preparation of the meal, the temperature and pressure employed, and is further varied according to the particular demands of the market for oil and cake respectively. In general, however, from 5 to 10 per cent. of oil remains behind in the press cake, which is usually of great value as a feeding stuff. When, however, the oil is more valuable, or when the cake is unsuitable for feeding purposes, this residual oil may be extracted from the cake by solvents.

The value of the cake as a feeding stuff lies in its content of proteins, albuminoids, carbohydrates, and oil.

Extraction.—The most efficient presses working with the highest obtainable pressures always leave from 5 to 10 per cent. of oil in the cake, because with increasing pressure the fine capillaries of the cake tend to close until a point is reached where the capillary tubes become so narrow that the oil can no longer

flow out. With the use of solvents, however, the quantity of oil remaining behind in the cake can be reduced as low as 0·5 per cent. on a practical scale.

The first successful attempt to extract oil from seeds by means of solvents was made by Deiss in 1856, who constructed an abstraction apparatus and employed as solvents bisulphide of carbon, chloroform and benzine. Great progress has been made during the last few years in the mechanical arrangement of extracting plant, particularly as regards the removal of the last traces of the solvent, nevertheless, it is unlikely that the extraction process will ever entirely supplant the press method, since for many purposes, such as the preparation of edible oils, the latter method must be used.

In the industrial extraction of fats and oils, comparatively few solvents have been hitherto employed, since the difficulties of using compounds of very high volatility in large quantities precludes the use of solvents such as ether, which gives admirable results in laboratory extraction. The more important solvents used are:—

1. Bisulphide of carbon.
2. Petroleum benzine.
3. Benzol.
4. Tetrachloride of carbon.
5. Acetone.
6. Chlorinated hydrocarbons, chief of which is ethylene hexachloride.

A short account of the mode of preparation, uses, and properties of the solvents is here given.

Bisulphide of Carbon is prepared by passing sulphur vapour over heated charcoal, condensing the vapours, and purifying the product by fractional distillation. The removal of the last traces of sulphur and other impurities may be effected by repeated distillation from vegetable oil.

Pure CS_2 is a limpid, highly refractive liquid of specific gravity 1·2922 at $\frac{0^\circ}{4^\circ}$ which boils under normal pressure at 46·2° C. Its latent heat of vaporisation at the boiling point is 83·81 calories, and specific heat ·250 calories. CS_2 gives off vapours

which form highly inflammable mixtures with air, and in certain proportions becomes explosive. A further disadvantage in the use of CS_2 is the poisonous action of its vapours when breathed. On standing for long periods, especially in sunlight, CS_2 decomposes, becoming yellowish in colour, with the liberation of free sulphur, which dissolves in the undecomposed bisulphide. At the same time carbon monosulphide is formed, according to the equation $CS_2 \longrightarrow CS + S$.

The purity of a specimen of CS_2 is ascertained by the following tests: —

1. When shaken with water containing neutral litmus, no acidity should be detected.
2. When shaken with metallic mercury, no blackening should occur (absence of dissolved sulphur).
3. 50 cub. centimetres, when carefully evaporated, should leave no residue.
4. When shaken with lead carbonate, no darkening should occur (absence of sulphuretted hydrogen).

Bisulphide of carbon is an admirable solvent for practically all fats, oils and waxes.

Petroleum Benzine.- This solvent consists of the low boiling distillate of petroleum, of which vast quantities are now placed on the market under various names. Benzine intended for use in oil extraction should not contain excessive quantities either of very low or very high boiling hydrocarbons, since the former are a source of loss and the latter are difficult to remove again from the extracted fat. A solvent benzine for the extract of dry material should not begin to boil below 45° C., and should distil over completely below 110° C. For the treatment of bones or waste fats containing quantities of water, however, it is essential to employ a solvent of higher boiling point than water in order that the moisture may be removed with the solvent vapours at the same time as the fat. Benzine is very highly inflammable, and the danger of explosion when mixed with small amounts of air is great. Its vapours when breathed produce narcosis.

The most important test of benzine intended for use as a solvent is the distillation test, but in addition it should show no free acid, and should not discolour when shaken with concentrated

sulphuric acid. 50 cub. centimetres gently evaporated on the water bath and finally heated at 110° C. in an open dish for ten minutes, should leave no residue.

Benzol is the low-boiling distillate of coal-tar, and possesses powerful solvent properties. It comes into the market as a light, limpid liquid of somewhat varying boiling point, according to the relative proportion of higher homologues present.

Three grades are recognised according to the percentage which distils over up to 100° C., viz.:

90's, *i.e.*, 90 per cent. by volume distils over at 100° C., specific gravity ·880/·883.

50's, *i.e.*, 50 per cent. by volume distils over at 100° C., specific gravity ·875/·877.

30's, *i.e.*, 30 per cent. by volume distils over at 100° C., specific gravity ·872.

Benzol vapours are highly inflammable, and produce objectionable physiological effects when breathed. When shaken with water containing litmus, the reaction should be neutral. When shaken with concentrated sulphuric acid, no darkening should occur.

When shaken with concentrated alkali solution, benzol should remain unchanged.

Acetone is prepared by the dry distillation of calcium acetate, and also is obtained from the products of the distillation of wood. The distillate purified by treatment with lime and fractional distillation is a colourless, inflammable liquid of specific gravity ·8138 at $\frac{0C}{4C}$, and boils under normal pressure at 57·1° C.

Acetone dissolves fats, waxes and resins very freely when dry, but possesses the disadvantage that, contrary to the above mentioned solvents, it is miscible with water.

Tetrachloride of Carbon is prepared by passing chlorine gas into bisulphide of carbon, when the following reaction takes place: $CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$.

The products are separated by fractional distillation, and the tetrachloride further purified by treatment with alkali. CCl_4 is a colourless, mobile liquid, of sp. gr. 1·6319 $\frac{0C}{4C}$, and boils under

normal pressures at 76·7° C. Its vapours are non-inflammable and non-explosive. When breathed, it produces partial anæsthesia. Three grades of commercial CCl_4 are recognised, viz.:

(a) Sulphur free; (b) technically pure; (c) purest. The technically pure contains small quantities of CS_2 and chlorine and sulphur-containing organic compounds. The purest CCl_4 is rarely employed industrially. 50 cub. centimetres evaporated on the water bath should leave no residue. Shaken with concentrated sulphuric acid, it should remain pale. The absence of halogen acid is shown by shaking with silver nitrate solution, when no cloudiness should appear.

Comparisons of Solvents.

An ideal solvent should possess the following characteristics:

(1) Its vapours should be practically non-inflammable, and when breathed should exert no injurious effects.
(2) It should preferably be a chemical individual, of such a boiling point as to permit of its being readily removed from the extracted fat.
(3) It should be chemically inert and stable.
(4) It should dissolve fats and oils in all proportions.
(5) Its specific heat and latent heat of vaporisation should be as small as possible, in order that a minimum consumption of steam will be required to distil it off.
(6) When recovered from a fat extraction, it should permit of simple purification.

Considered from these points of view, no one solvent can be said to be perfect for all purposes; and the choice of compounds used will depend primarily upon the type of extraction apparatus and the nature of the product required to be extracted. This latter consideration applies with particular force to the preparation of oils intended for use as foodstuffs or the manufacture of high grade soaps. Bisulphide of carbon, although extensively and successfully used for the extraction of products like bone grease, cannot be applied for the preparation of edible and best quality soap-making oils, since the danger of leaving traces of sulphur in the finished product is so great. Edible oils extracted by this solvent, unless particular care has been taken, possess a

disagreeable smell and taste, and soaps made from the oils tend to darken in colour on storing. Again, it is found that the presence of large masses of non-volatile substances retards very powerfully the removal of compounds of relatively high boiling point, and in this respect benzine possesses some disadvantages.

The quantity of steam required to evaporate the solvent is of course proportional to its specific and latent heats.

To illustrate the wide variation in this respect between solvents the following figures are given:—

	Specific heat.	Latent heat of vaporisation.
CS_2 . . .	·260 calorie at 80° C.	83·8 calories
Solvent benzine .	·480 to ·510 „	70 to 79 „
CCl_4 . . .	·216 „	46·6 „

The extraction process resolves itself into three operations in addition to the preliminary treatment.

(1) The treatment of the raw material with the solvent.

(2) The removal of the solvent from the fat solution.

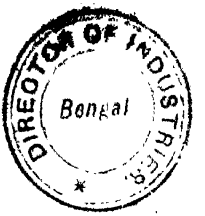
(3) The removal of the last traces of solvent, from the extracted residue and fat.

The preparation of the seed for extraction by solvents is similar to that described for expression, save that the meal must be coarser. When the temperature of extraction is below the boiling point of water it is necessary to remove any excessive quantity of water, which may be present in the raw material (sewage, garbage, fat, etc.), but, for the majority of seeds, the water naturally present does not materially influence the extraction. The solvent benzine which boils between 100° and 120° C., possesses the advantage that it may be used for wet material, since the vapours, being above the temperature of boiling water, removes the moisture together with the fat. The apparatus employed for extraction resembles in many respects that employed in the laboratory. A simple type is that in which the meal is spread on trays through which the solvent percolates. The

extraction may be carried out at the ordinary temperature, warm, or by means of the heated vapours of the solvent.

When the extraction is considered to be complete, the solution of fat is run off into a kettle or still, the solvent evaporated off by indirect steam, and the vapours condensed by passing through tubes cooled by water. The condensed solvent is then ready for use on a fresh batch of raw material. A continuous system of extraction is sometimes employed after the manner of Soxhlet's laboratory extractor. The last traces of solvent in the fat and residue are removed by blowing a current of steam through the mass.

The solvent process finds large application in the extraction of rough fatty matter from bones, and the residues of certain manufacturing processes. In some cases the raw material may be extracted direct, but more generally a preliminary drying and disintegrating is necessary, since, as mentioned above, if the substance to be extracted is very wet, the fatty matter is protected from the action of the solvent by a film of moisture, which must be got rid of by drying the raw material in a current of hot air, or by employing a solvent of high boiling point.



CHAPTER IV

IMPURITIES OCCURRING IN CRUDE OILS AND FATS AND THE TECHNICAL METHODS OF REMOVING THEM

The raw fat or oil obtained by any method of preparation is rarely chemically pure. By working on perfectly fresh, raw material, however, and taking extreme precautions to render or extract at low temperatures, it is possible to obtain a portion of the fat or oil contained in the material of a high degree of purity. But this is not often possible, is at all times somewhat costly, and is only necessary when the fat is intended for some special purpose, such as the manufacture of edible oils, or butters.

In the great majority of cases the raw fat contains impurities of a more or less deleterious nature, which must be subsequently removed by submitting the oil to a process of refining.

Then purification of the fats and oils is one of the most important and difficult problems in the industry, and is only rendered possible by a knowledge of the nature and properties of the impurities. It is impossible to devise any specific process of refining which shall be applicable to all cases, but each problem must be dealt with on its own merits. At the same time, however, broad definite methods of refining can be indicated, since the same kind of fat obtained in the same way always contains similar impurities. The degree of purity which it is desired to attain will depend in all cases, of course, upon the uses to be made of the refined article. For example, burning oils must be free from inorganic matter, which causes the wick to char, edible oils and fats must be devoid of unpleasant odour or taste, while oils intended for use in the soap industry must not contain excessive quantities of unsaponifiable matter, although free fatty acids are no objection.

The impurities have their origin in three chief sources:—

(1) The process of obtaining the oils.

(2) The apparatus employed.

(3) The faulty storage of the seeds, tissue, or crude oil.

(1) The quantity and nature of the foreign matter introduced by the process of extracting the oil varies somewhat with the particular method employed.

In the "rendering" of the fat, easily decomposable products are formed—fatty acids, acrolein, hydrolytic products, not only of the fat, but also of the animal fibres, such as organic bases, aldehydes, acids, hydrocarbons, etc., from the proteins, all of which dissolve in the molten fat and impart to it objectionable odours, tastes and colours.

In the "expression" process the oil becomes charged with the watery fluids of the cells, which are pressed out at the same time, and also with the protein constituents of the plant or animal. The extraction by solvents process yields a product containing practically no mechanical impurities, but since the solvent can dissolve dyes and odoriferous principles, the extracted fat is not free from colour or flavours. Further, the solvent action of different solvents for such foreign matter is variable, and consequently the same fat when extracted by different solvents is obtained in varying degrees of purity.

(2) The free fatty acids which occur in all raw oils and fats act upon the metal walls of the tanks, presses, pumps, etc., forming metallic soaps, which dissolve in the oil. At the same time bits of filter cloth, press bag, and abrasive metals from the extraction plant, mingle with the oil.

(3) During storage, particularly if insufficient care, attention be paid to the proper ventilating, drying, etc., of the storehouse, the oil becomes rancid. A satisfactory refining process can only be devised when the nature of the impurities, and the way in which they are present with the oil, is known. We shall, therefore, consider these factors at some length. The impurities, which are either (*a*) mechanically mixed or emulsified, or (*b*) dissolved in the oil, may be broadly divided into two classes, namely, (1) organic and (2) inorganic substances.

Among the organic, the more important are proteins, carbohydrates, gums, resins, enzymes, soaps, glycerine, lecithin, and

hydrocarbons, while among the inorganic, one has to deal with water, metallic salts, etc.

The proteins may be divided into three classes, simple proteins, conjugated proteins, and albuminoids, all of which may be present in the crude oil. In general the proteins are soluble in water, better in dilute saline solutions. All proteins exhibit a tendency to coagulate, the coagulated body generally being insoluble, This coagulation is brought about by heat, the action of mineral acids, and concentrated salt solutions, best of which is ammonium sulphates. A most important representative of the conjugated proteins, which occurs in many oils, is the compound mucine, which is a compound of a simple protein with a carbohydrate. Compounds like this possess a powerful emulsifying influence and their presence in a raw oil is indicated by the formation of persistent emulsions, when the oil is shaken with water.

The albuminoids are a group of substances similar in some respects to the proteins.

The albuminoid collagen is the substance of which the white fibre of connective tissue is composed, and may be expected, therefore, to be mixed with oils obtained by pressing animal tissue.

It is not quite certain whether the proteins are dissolved in the oil in the true sense of the term, but it is probable that they are present in the form of pseudo solutions, as explained on p. 54. From the above description, the most satisfactory methods of removing the proteins will be gathered. The object in all cases being to render them insoluble in the oil, and then to remove them. This may be brought about, as we shall see later, by warming, or by treating the oil with concentrated salt solutions or mineral acids, all of which methods result in a more or less perfect coagulation of the proteins. The precipitating proteins always bring down with them the bulk of the suspended impurities.

The vegetable and animal gums are carbohydrate-like bodies, very prevalent in linseed and other oils. These substances are soluble in water, are powerful emulsifiers, and inhibit the precipitation of metallic hydrates by alkalies; they may be removed, however, by treating the oil with alkali or washing out with salt

solutions. It is important to notice that precipitates in gummy solutions show colloidal characters, and so cannot be separated by filtration.

Ferments and Enzymes.—These substances, which are of a protein-like character, are powerful catalysers, hydrolysing or oxidising the oil according to their specific property.

Among the more important enzymes which have been detected in oils are lipase, a most powerful fat splitting enzyme occurring in castor seeds, and myrosin emulsing in mustard seed oil.

In olive oil the oxydase olease has been detected. It is capable of converting olive oil slowly into CO_2 acetic and sebacic acids. All enzymes are killed at certain temperatures and also by strong acids or alkalies. Soaps, free fatty acids, glycerol, lecithin (a phosphorus compound) and resins are present in varying amounts in the crude oil, from which they may be separated by treatment with water and alkaline solutions.

The lipochromes, chlorophyll, etc., are nearly always present, and may generally be destroyed by bleaching. Our knowledge of the constitution of the flavour and odoriferous substances present in the oil is but vague.

Inorganic Impurities. — Some oils, especially linseed, can directly dissolve salts, but, as a rule, the inorganic material is dissolved in the water, which is intimately mixed with the oil.

Quite apart from the importance of purifying the oils for technical purposes, a refined oil deteriorates much less on storage than an impure oil, since enzymic action, which is assisted by the presence of water, brings about slight hydrolysis and decomposition of the fat or oil.

The methods of purification have for their object—

(1) The removal of mechanically-mixed substances.
(2) The dissipation of emulsions.
(3) The removal of dissolved impurities.
(4) The removal of free fatty acids.
(5) Bleaching and removing objectionable odours.

Mechanical Impurities may frequently be removed by simply allowing the oil to stand in a warm tank for two or three days, when the grosser particles fall out, and are deposited at the bottom as a precipitate. If, however, the particle in suspension

is very fine, and the oil viscous, precipitation will not take place for an immense period of time. In such cases one aims at either producing a precipitate in the oil or filtering through earth. The former case is particularly interesting, and illustrates a phase of surface action.

The suspended particle is attracted towards the grosser particle of precipitate, and so a large aggregate is formed, readily acted upon by gravity, and consequently quickly falling. The substances employed for producing this effect may be oilcake meal, fuller's-earth, Kieselguhr, aluminium hydrosilicate, or animal charcoal, all of which substances exert this surface action. The powder is thoroughly mixed with the oil, and the mixture then allowed to stand until separation occurs, or filtered free from the precipitate.

Emulsions.—An emulsion is a mixture of two immiscible liquids, in which one of the liquids is distributed throughout the other in the form of fine drops. The emulsions with which we have to concern ourselves are formed from fine drops of water, or saline solutions suspended in oil. Such emulsions show little or no tendency to settle, and are always dull and opaque. Without going into detail on the nature of emulsions, we may point out that this again is a phenomenon of surface action, depending upon the relative surface tensions of the two liquids towards one another, the emulsion being stable until a certain change is brought about in these relative tensions. The most frequent emulsifiers are soaps, alkalies, gums, and mucines. It is almost impossible to dissipate an emulsion by simple filtration, unless the filter material is composed of hygroscopic substances. Occasionally it suffices to warm and blow air through the heated oil, but more satisfactory is treatment with an acid.

Substances Dissolved by the Oil.—The removal of impurities of this class can only be effected on a practical scale by treating the oil containing them with reagents, which render them insoluble in the oil. The most suitable reagent for this purpose is concentrated sulphuric acid, which attacks soluble proteins, resins, gums, etc., decomposing them and forming a charred product no longer soluble in the oil. The process is carried out as follows :—

To the cold oil contained in a lead-lined vat, provided with mechanical agitators, about 1 per cent. of its weight of concentrated sulphuric acid of 66° Be. is slowly added with constant agitation. The mixture is thoroughly stirred for from 1½ to 5 hours, then allowed to rest, and the acid layer drawn off (foots). The oil is then washed free from acid by water, the water drawn off, and the oil allowed to stand to clarify. The effect of the acid is to decompose soaps and proteins, break down emulsions, and destroy enzymes and ferments.

The acid foots drawn off are a thick viscous mass, containing, besides the impurities, some fat and sulphonated fatty acids.

On boiling with water the sulphuric acid is removed, and these substances float on the surface, may be skimmed off, and subsequently treated for the preparation of commercial products.

At the same time, the sulphuric acid attacks the oil to a slight extent, forming sulphonic acids, which decompose in the subsequent treatment with hot water, into hydroxy acids.

If the acid refining is wrongfully carried out, *i.e.*, at too high a temperature, or too great a concentration of acid, the resultant oil is dark coloured, an error which cannot be remedied by bleaching.

Somewhat similar results can be obtained by the use of other dehydrating agents, such as anhydrous zinc chloride.

Refining by Basic Reagents.—Of equal importance to the sulphuric acid is the treatment with concentrated solution of alkalies, the most usual being caustic soda, a process introduced by Gwynne in 1843, and improved by Evrard in 1855. The effect of this reagent is, on the one hand, like sulphuric acid, to decompose and remove proteins, etc., but, at the same time, it forms soaps with the free fatty acids and resins which dissolve in the aqueous solution, and so are drawn off.

This process is also of value in removing suspended matter, since the soaps are formed throughout the oil in flocks which enclose and bring down the particles.

Two methods of procedure are employed: (*a*) treatment with concentrated lyes, (*b*) treatment with dilute lyes.

In the former case it is customary to employ about 2 or 3 per cent. of lyes of 36° Be., while in the latter case over 10 volumes of

lyes per 100 volumes of oil of 12°—15° Be. is employed. In all cases, however, the quantity and concentration of lyes needs modifying according to the purity of the raw oil. The mixing is effected at 40°—50° C., and when the action is judged to be complete the mass is allowed to stand until separation occurs. The under layer of caustic lyes containing the soaps and other impurities, is withdrawn, and there remains a sliny intermediate layer, above which floats a more or less clear oil; the intermediate layer is allowed to subside, as far as possible, and is in some cases assisted by centrifuging the mass. The supernatent oil is washed with water until free from alkali, and allowed to stand to clarify. The art of the refiner consists in so adjusting the various factors that, while complete purification is attained, minimum saponification of the fat shall occur, and the formation of persistent emulsions be avoided. To obviate this latter difficulty it has been suggested to mix common salt with the lyes, since this tends to hinder emulsification. It is not usual, however, to adopt this procedure, since a perfect mixing or emulsification of the oil and lyes, in the first case, is essential, and it is always possible, by choosing suitable concentrations, to attain a more or less rapid separation on standing. Various modifications, more or less of a transitory nature, such as conducting the process under pressure of an indifferent gas, or the employment of ammonia, are occasionally employed.

By far the largest quantity of oil on the market is refined by the caustic alkali treatment, but where the removal of free fatty acids is the chief consideration, it is possible to employ lime or magnesia in place of caustic, and to remove the resultant insoluble soaps by passing the mixture through a filter press.

The alkaline liquors (foots) contain a quantity of soap and oil which is recovered by acidifying and then removing the fatty layer which rises to the surface. Where both acid and alkali refining is carried out in the same works it is customary to mix the acid and alkali foots to produce a neutral or faintly acid mass, from which the fatty matter readily separates.

Bleaching, and Removing Objectionable Odours.

Raw fats and oils which owe their colour to the presence of naturally-occurring lipochromes, may generally be bleached to a

fine whiteness. Two methods are employed, namely (*a*) adsorption of the colour stuff, (*b*) destruction of the colour.

If a solution of colour stuff in water is shaken with fine earth or charcoal, and then allowed to stand until the solid matter subsides, it will be found that a quantity of the colour stuff has left the solution, and "adsorbed" on to the powder.

In the same way the colour stuff which is dissolved in an oil or molten fat, may be removed, by shaking with a powder. The decolourising powders usually employed are blood, charcoal, Kieselguhr, china clay, and Florida earth (aluminium magnesium hydrosilicate).

During the process of treatment with sulphuric acid, or caustic lyes, a certain amount of colour is destroyed, but a more perfect bleaching is ensured by treating the oil with either direct or indirect oxygen. In some cases the destruction of the colour stuff may be brought about by blowing air through the oil, heated to about 100° C. This is a process in which the colour is destroyed by the oxygen of the air. Similar bleaching action ensues in some cases when the oil is submitted in thin layers to the action of the air, in the presence of strong sunlight, a process of natural bleaching once largely employed in the preparation of the colourless varieties of linseed oil.

The chemical mechanism of this process appears to consist in the intermediate formation of ozone, or hydrogen peroxide, by the action of ultraviolet light on oxygen of the air mixed with water vapour. The process, however, is slow and expensive, and has been almost entirely superseded by the employment of chemical oxidising agents. Of these two types are employed, on the one hand, the peroxides of the metals, to which has recently been added a number of organic peroxides (benzoyl peroxide, acetyl peroxide, etc.), while on the other hand, advantage is taken of the inorganic bichromates, and permanganates which liberate nascent oxygen when treated with acids. Chlorine obtained from chloride of lime by treatment with acid is also employed, the chlorine liberating oxygen from the water.

The mechanism of these processes is illustrated in the following equations :—

$$Na_2Cr_2O_7 + 5\,H_2SO_4 = 2\,NaHSO_4 + Cr_2(SO_4)_3 + 4\,H_2O + 3O,$$

or $$Na_2Cr_2O_7 + 4\,H_2SO_4 = 2\,NaCr(SO_4)_2 + 4\,H_2O + 3O$$

chrome alum.

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5O.$$

(a) $$CaCl_2 + Ca(OCl)_2 + 2\,H_2O + 2\,H_2SO_4 = 2(CaSO_4 2\,H_2O) + 2\,Cl_2$$

chloride of lime

(b) $$Cl_2 + H_2O = 2\,HCl + O.$$

The bichromate bleach, which is the most general process, is carried out as follows:—

For each 100 lbs. of oil about 1 lb. of bichromate is employed. The bichromate is dissolved in 3—4 times its weight of water and the calculated quantity of sulphuric acid previously diluted to about 20 per cent. strength is added to the solution.

The oil and liquor is mixed thoroughly for ½ to 1 hour and the finely divided emulsion then left to separate.

After drawing off the spent liquor the oil is washed well with warm water until free from acid and allowed to clarify.

It is important to conduct the operation at as low a temperature as possible in order to avoid attacking the oil itself.

The bleach by chloride of lime is similarly conducted, the dilute solution of chloride in acidulated water being intimately mixed with the oil when the two reactions indicated by the equations go on side by side.

Occasionally it is found to be impossible to bleach an oil or fat by either chemical or physical processes, owing to the extreme inertness of the colouring matter. In such cases it becomes necessary to saponify it and then distil the fatty acids in steam, whereby good white products can usually be obtained equally valuable for many purposes as the original glycerides.

Objectionable odours which are usually due to the presence of volatile matter can generally be eradicated by boiling the oil with water, dilute alkaline solutions, or blowing low pressure steam through it. Many oils can be partially deodorised by agitating with the usual filter or bleach materials, but others again, notably the fish oils, retain their unpleasant smell most persistently. The peculiar fishy odour of most marine animal oils appears to be due the presence of quite minute amounts of amines and organic phosphorous compounds. So far it has not been practical to

remove this smell by the ordinary methods, but the solid products obtained by catalytic reduction of fish oils are almost odourless.

It will be gathered from the foregoing remarks that each reagent or purifying process brings about a number of effects besides that for which it was primarily employed. For example, alkaline lyes not only remove free acids, but also destroy ferments and coagulate proteins, while sulphuric acid withdraws any water which may be present in addition to its other action. Now each individual raw oil contains its own special group of impurities, and when one knows the nature of these foreign bodies it is easy to postulate how many of the impurities could be removed at once by each of the standard processes and reagents described; that operation will then be selected which can remove the greatest number of impurities in one step with the minimum injury to the oil.

CHAPTER V

COMPOSITION AND PROPERTIES OF THE SAPONIFIABLE OILS AND FATS IN GENERAL

On boiling the saponifiable oils, fats and waxes with strong alkaline solutions, or by subjecting them to the action of superheated steam, decomposition of the esters occurs with the separation of the acid and basic parts of the molecule.

The acids are known as fatty acids, while the basic substance is an alcohol—from the true fats and oils invariably glycerol from the waxes, various monobasic alcohols. Altogether representatives of nine different series of organic acids have been isolated from the natural fats and waxes. They may be classified according to their chemical constitutions as follows:

(1) **Monobasic Saturated Acids of the Acetic Series.** General formula $C_nH_{2n+1}COOH$. Members of this series occur in every known fat and oil. The lower homologues are pungent liquids soluble in water and volatile in steam. As the molecular weight increases they become less soluble in water, less pungent, and weaker in acidic properties. Members possessing twelve or more carbon atoms are practically insoluble in water, odourless, and of a distinct oily or fatty nature. It is usual to divide the series into two groups, according to their solubilities and volatilities; the homologues containing less than seven carbon atoms being called soluble acids, while the higher members constitute the insoluble fatty acids.

The term "volatile fatty acids" is usually applied to those members below lauric acid $C_{11}H_{23}COOH$. At ordinary temperatures the higher members are solids. Owing to their saturated structure, the members of this series are characterised by great stability towards reagents, and may be distilled in vacuo undecomposed even up to twenty carbon atoms. The more important homologues and their constants have been given in Chapter I.

A most important property of the fatty acids is their ability to form eutectic mixtures with one another, *i.e.*, if a mixture of saturated fatty acids of high molecular weight be melted, and then allowed to cool gradually, at a certain temperature crystals begin to form which possess a definite composition; for example, if a mixture of stearic and palmitic acids is melted and allowed to cool, it is found that at 56·4° C. crystals separate which possess the composition 47·5 per cent. stearic and 52·5 per cent. palmitic acid. Such a mixture is most difficult to separate into its constituents, and behaves as though it were a separate compound; in fact, for a long time this mixture was thought to be an acid of formula $C_{16}H_{33}.COOH$.

Further, mixtures of the fatty acids frequently melt at lower temperatures than either of their constituents, *e.g.*, stearic acid melts at 69·32° C. and palmitic at 62·62° C., while a mixture containing these acids in the proportions 29·76 per cent. and 70·24 per cent. respectively melts at 54·82° C. All the acids of this group form salts with the alkalies (soaps), alkaline earths and metals.

The potash and soda salts are soluble in water, but the compounds with the heavy metals are insoluble. The higher fatty acids are readily soluble in ether and most organic solvents. They are difficultly soluble in cold, but freely in hot alcohol.

(2) **Unsaturated Monobasic Acids** containing one double bond —oleic acid group.

General formula $C_nH_{2n-1}COOH$.

The lower members of this group rarely occur in the natural oils, but the higher homologues are universally present. The best known representatives are given in the table on page 25.

Since they contain a double bond in the molecule, these acids readily absorb and combine with two halogen atoms, and when treated with a solution of potassium permanganate, hydroxyl groups are formed at the double link, giving rise to the dihydroxyl acids, *e.g.*, oleic is converted into dihydroxy stearic, according to the following equation :—

$$CH_3.(CH_2)_7.CH=CH-(CH_2)_7.COOH \xrightarrow[KMnO_4]{\text{alkaline}} CH_3.(CH_2)_7.\underset{OH}{CH}-\underset{OH}{CH}.(CH_2)_7.COOH$$

A peculiarity of the unsaturated acids is their behaviour when treated with nitrous fumes, or solutions of sulphites. Under the influence of these reagents solid isomers are formed from the liquid oils; thus oleic acid passes into its isomer elaidic acid. Most characteristic of the unsaturated acids is the solubility of their lead salts in ether, a property which distinguishes them from the saturated acids and forms a convenient method of separating them from admixtures with the latter. The unsaturated acids can be reduced to saturated by hydriodic acid, and much attention has of late been directed to the reduction of these acids on a practical scale. A number of patents have been taken out purporting to effect the reduction by passing hydrogen gas over mixtures of the acids and finely-divided nickel which acts as a hydrogen carrier or catalyst.

(3) **Unsaturated Acids** containing two double bonds (linolic series), general formula $C_nH_{2n-3}COOH$.

These acids are characterised by their ability to combine with four halogen atoms, and pass by oxidation with potassium permanganate into hydroxy acids containing four hydroxyl groups, the most important member, linolic acid, $C_{17}H_{31}COOH$, being converted into tetrahydroxy stearic or sativic, $C_{17}H_{31}(OH)_4COOH$. They readily absorb oxygen from the air, forming hard resinous products (drying). With nitrous acid they are not converted into solid isomers after the manner of the oleic series. They form salts with the alkalies and metals; the lead salts are soluble in ether. The lower members of this series do not occur in oils, but apparently only linolic acid, $C_{17}H_{31}COOH$, and its isomers. They are:—

Acid.	Formula.	Occurrence.	Melting point. °C.
Linolic . .	$C_{17}H_{31}COOH$	All semi-drying and drying oils, also many non-drying oils	below −18° C.
Tariric . .	„ „	Picramnia seeds	50·5° C.
Telfairic .	„ „	Kœme oil	about 6° C.
Elæomargaric	„ „	Tung oil	43 to 48° C.

(4) **Unsaturated Acids** containing three double bonds.

Linolenic series. General formula $C_nH_{2n-5}COOH$.

The representatives of this series containing eighteen carbon atoms occur in considerable quantity in the drying oils.

They are characterised by great instability, oxidising and resinifying (polymerising) with great readiness when exposed to the air.

They combine with six halogen atoms, and pass on oxidation with permanganate into hexahydroxy acids. The three best-known isomers are:—

(*a*) Linolenic, $C_{17}H_{29}COOH$, occurring in all drying oils,

(*b*) Isolinolenic, probably occurring as a glyceride in linseed oil, and

(*c*) Jecoric, which appears to occur in sardine oil.

The members of this series have not been investigated very completely, and their constitution is unknown. The methods of investigation hitherto employed have been to convert them into their corresponding hydroxy acids or brom compounds, the constitution of which is then studied.

On exposure to air the members of the linolenic series absorb oxygen and undergo a curious change with the formation of hard films. This property is of immense importance in the arts, and is made use of in the manufacture of paint vehicles, linoleum, printers' ink, and a variety of products.

The hard oxidation product formed is insoluble in most organic solvents, and appears to be produced by the combined effect of oxidation and polymerisation. This reaction will be further discussed in the section on Oxidised Oils.

(5) **Unsaturated Acids** containing four double bonds.

Clupanodonic series. General formula $C_nH_{2n-7}COOH$.

Very few acids of this series have been isolated and studied, and owing to the rapidity with which they oxidise in the air, their investigation is intensely difficult. Three representatives have been described as occurring in the fish liver oils. They are:—

(*a*) Isanic acid, $C_{13}H_{19}COOH$.

(*b*) Therapic acid, $C_{16}H_{25}COOH$, which probably is present in cod liver oil.

(*c*) Clupanodonic acid, $C_{17}H_{27}COOH$, occurring in considerable quantities in Japanese sardine, herring and whale oils.

By treatment with bromine the latter acid forms an octobromide of formula $C_{17}H_{27}Br_8COOH$.

Lewkowitsch considers "that jecoric acid and therapic acids are nothing else but more or less impure clupanodonic."

(6) **Unsaturated Acids,** containing one hydroxyl group. Ricinoleic series. General formula $C_nH_{2n-2}(OH)COOH$. The only member of importance is ricinoleic acid, the chief constituent of castor oil, $C_{17}H_{32}(OH)COOH$. This acid absorbs two atoms of halogen, thus proving the existence of a double bond, and on shaking with permanganate is converted into an acid containing three hydroxyl groups.

By the action of sulphuric acid on ricinoleic acid and its glycerides, products are obtained known as sulphonated oils (Turkey Red oils).

(7) **Saturated Acids** containing two hydroxyl groups. Only one acid of this group has been detected in the natural fats, namely, dihydroxystearic, $C_{17}H_{33}(OH)_2COOH$. This acid was isolated by Juillard from the glyceride occurring in castor oil.

(8) **Dibasic Acids**, of the formula $C_nH_{2n}(COOH)_2$. Japanic acid, $C_{20}H_{40}(COOH)_2$, from Japan wax, is the only known member of this series.

(9) **Cyclic Acids.**—Chaulmoogric series. These acids contain a closed ring in their carbon chain. The only member of importance is chaulmoogric acid, $C_{17}H_{31}COOH$, isolated from chaulmoogra oil. It contains one double bond.

Alcohols.

The basic fraction obtained from the hydrolysis of the oils, fats and waxes are alcohols; from the fats only, the tribasic alcohol glycerol.

Glycerol was discovered in 1779 by Scheele, and was known to the early chemists as "Scheele's Sweet Principle of Fats." It is an essential constituent of all saponifiable fats and oils, from which it is obtained in great quantities in the soap and candle manufacture. In its pure state glycerol is a colourless, odourless

syrupy liquid with an astringent sweetish taste, of specific gravity 1·2604 at 20° C. On cooling in a mixture of snow and salt, it solidifies to a mass of rhombic crystals which melt at 17° C. and boil at 290° C. It is miscible with water in all proportions, but is difficultly soluble in ether, chloroform, petrol or carbon bisulphide, and so cannot be extracted from its watery solution by these solvents. Towards chemical reagents glycerol is fairly reactive, dehydrating agents in the hot, converting it into the corresponding aldehyde acrolein, a volatile substance with a most penetrating irritating odour.

$$\begin{array}{lcl} CH_2.OH & H_2SO_4 & CH_2 \\ | & \dashrightarrow & \| \\ CH.OH & & CH \\ | & & | \\ CH_2.OH & & CHO \end{array}$$

Under certain conditions glycerol can form esters with the mineral acids. Its compound with nitric acid is of great practical importance (nitroglycerine), but on heating with nitric acid it suffers decomposition into formic, glycolic, oxalic and carbonic acids.

Alkaline permanganate brings about a similar decomposition. Glycerol cannot be distilled at the ordinary pressures without decomposition, but may be purified by distillation in a vacuum.

In the natural waxes there occur a number of **mono and dibasic alcohols**, and in the unsaponifiable portion of the fats a few cyclic derivatives are present. At least three series of monobasic and one of dibasic alcohols have been detected.

(1) **Saturated Alcohols of the Methane Series.**— General formula $C_nH_{2n+1}OH$. These alcohols occur in the waxes; they are chemically very stable, and may be boiled with alkaline or acid solutions without change. On distillation they are converted into the corresponding fatty acids, and chromic acid oxidises them to fatty acids containing the same number of carbon atoms in the molecule. The three most important members are:

(*a*) Pisang ceryl alcohol, $C_{13}H_{27}OH$, found in pisang wax.

(*b*) Cetyl alcohol, $C_{16}H_{33}OH$, which forms, in combination with palmitic acid, the principal constituent of spermaceti, and

(c) Octodecyl alcohol, $C_{18}H_{37}OH$, also found in spermaceti.

Of considerable importance are carnaubyl alcohol, $C_{21}H_{49}OH$, occurring in woolwax, and ceryl alcohol, $C_{26}H_{53}OH$, found in Chinese wax, wool fat and carnauba wax. The acetate of the latter, which serves to characterise it, melts at 65° C. Myricyl alcohol, $C_{30}H_{61}OH$, in combination with palmitic acid, is the chief constituent of beeswax. Its acetate melts at 73° C.

(2) **Unsaturated Alcohols** containing one double bond.

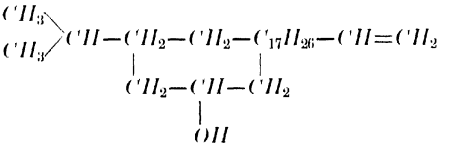
General formula $C_nH_{2n-1}OH$. A few derivatives of this series have been detected in the waxes, but their investigation is very incomplete. Lewkowitsch expresses the opinion that the "unsaturated alcohols occurring in sperm oils belong to this series."

(3) **Saturated Dibasic Alcohols** of the series $C_nH_{2n}(OH)_2$.

The most important derivative is cocceryl alcohol, $C_{30}H_{60}(OH)_2$, obtained in crystals melting at 101° C. from the wax of the cochineal.

(4) **Cyclic Alcohols.**—The cyclic alcohols are divided into two groups, namely, (1) derivatives of the cholesterol group which abound in the unsaponifiable material always associated with oils and fats of animal origin; and (2) the phytosterol group, derivatives of which occur in every known vegetable oil.

The constitution of cholesterol is still in doubt, but it would appear to possess the formula



Cholesterol is soluble in hot alcohol from which it crystallises in thin plates of characteristic appearance (under the microscope).

When obtained in an anhydrous state it melts at 149 to 150° C. As a confirmatory test for cholesterol, dissolve a few crystals in 2 to 3 cub. centimetres of chloroform, and add an equal volume of strong sulphuric acid. On shaking, the solution becomes first red, changing rapidly to purple. The purple colour changes

to blue, green and then yellow, when a few drops of the solution are poured into a porcelain plate owing to the absorption of water from the air.

A compound of similar empiric formula occurs in wool fat, and is known as isocholesterol, melting point 136 to 137° C.

Phytosterol, occurring in all plant oils, is probably a mixture of several substances of an alcoholic character whose constitution is unknown. Its more important properties are described under Analytical Methods.

Besides simple triglycerides, a large number of mixed glycerides have been detected and isolated from natural fats, viz., oleodipalmitin, oleodistearin, dipalmitostearin, etc. No natural fat or oil consists of one individual pure glyceride, but invariably a number of different fatty acids are present. The glycerides of the lower fatty acids, such as butyrin, caproin, laurin, etc., frequently occur, but only in relatively small quantities, the preponderating glycerides being formed with acids of from 16 to 20 carbon atoms. In fact, it is only when we arrive at high molecular weight acids that the true fatty nature of the glycerides is manifest. In addition to the saponifiable glycerides proper, all oils contain a small amount of unsaponifiable matter, consisting mainly of cholesterol or phytostearol, various waxes, resins, colour stuffs, essential oils, etc. Such unsaponifiable matter is to be regarded as an essential constituent of the oil, as distinct from other kinds of unsaponifiable material added for adulteration or other purposes. The average percentage of unsaponifiable matter present in a few typical oils and fats is—

Olive oil, ·70	Tallow, 0·5
Linseed oil, 0·8	Lard, 0·25
Cotton seed oil, 1·6	Whale oil, 1·5
Cocoanut oil, 1·5	Fish oil, 1·3

Physical Properties.

Mixtures of pure glycerides are odourless, colourless and tasteless, but the purest oils and fats obtainable in commerce all possess characteristic and distinctive colours, odours and flavours. These colours and odours are due to the presence of exceedingly minute traces of foreign substances mixed with small amounts of

volatile and free fatty acids. Olive oil, for example, owes its greenish tint to the presence of chlorophyll, and its odour and flavour to minute quantities of esters of the lower fatty acids and monohydric alcohols, etc. The distinctive smell of castor oil appears to be due to traces of aldehydes (œnanthylic aldehyde) and lower acids, while the fragrant perfume of cocoanut oil has been ascribed to certain ethereal oils contained in its unsaponifiable matter. All vegetable oils contain notable quantities of free fatty acids, the percentage varying with the age of the seeds and the way in which they have been stored. Animal fats, however, contain in the fresh state very little free acids, and may be said to consist almost wholly of neutral glycerides. Although the composition of an oil or fat obtained from some specific plant or animal remains sufficiently constant to serve as a means of characterising the oil, yet considerable variation in composition is found in the oil from any one species of plant or animal according to the climate and soil in which it is grown, or the age and food of the animal from which it is obtained. This point will be further brought out in the chapter on the individual oils. Oils and fats have a wide range of consistency, some being fluid at 18° C., while others remain solid up to 50° C. It is customary to speak of those which are liquid at ordinary temperatures as "oils," while the term "fat" is applied to those which are solid at ordinary temperatures; but no sharp line of demarcation is possible, since many substances possess a buttery or semi-solid consistency at ordinary temperatures. Such oils may be liquid on a warm summer's day or in a tropical climate, while during the winter they may congeal to a solid fat. When some liquid oils are gradually cooled solid glycerides separate in a more or less crystalline state, and may be filtered or "centrifuged" free from the liquid portion. This process is used in the industry, and is known as "demargarinating." The solid glycerides deposited are known as "stearines." [1]

This phenomenon indicates that the liquid oils are really

[1] The words "stearine" and "olein" are used in a technical sense to describe all solid and liquid portions respectively which may be separated from an oil or fat by demargarination and consequently possess a different meaning to the words stearin and olein, which represent in scientific language the "glycerides" of stearic and oleic acids respectively.

solutions of solid in liquid glycerides. The semi-solid and hard fats may be looked upon as solid solutions much in the same way as we nowadays consider metallic alloys. The specific gravity of the fatty oils varies from ·910 to ·950 at 60° F., and the coefficient of expansion per degree F. is about ·0007.

With the exception of castor (which possesses very high viscosity), the saponifiable oils and molten fats are moderately limpid liquids with from ten to twenty times the viscosity of water at 20° C. In this respect they differ from the high-boiling unsaponifiable oils, many of which are 300 times more viscous than water at 20° C. All fats and oils are bad conductors of heat and electricity. The specific heat may be calculated by dividing the percentages of carbon, hydrogen and oxygen contained in the oil by the atomic weights of these elements respectively, and multiplying the quotients by the known values for atomic heats, viz., $C=1·8$, $H=2·3$, $O=1·0$.

The values for all the oils lie between 0·1 and 0·5.

One of the most characteristic properties of oils is their ability to spread and form films on any liquid or solid surface which does not react chemically with them. This phenomenon of spreading, or "wetting" as it is called, is of great importance, and is due to the low surface tension between a surface of oil and other liquid or solids. Most of the industrial applications of the oils and fats can be traced to the utilisation of this principle, which has only recently been recognised, and so far but little studied. Pure chemical compounds always melt suddenly at a fixed temperature called the melting point. Since the fats, however, are not chemical individuals, but mixtures of glycerides, they show no sharp melting or solidifying point. When a fat is slowly heated at a certain temperature it begins to soften, but does not become liquid till a higher temperature is reached. The first temperature of softening is sometimes called the point of "incipient fusion," as compared with the temperature with which the whole mass becomes liquid or "point of complete fusion." A few of the fats show a double melting point; that is to say, on heating they first melt, then solidify again, and on further heating once more fuse.

The solidifying temperature of an oil or molten fat is always a

few degrees lower than the melting point, and is generally somewhat more sharply defined than the melting point.

The glycerides possess no boiling point, *i.e.*, they do not boil undecomposed even in high vacua, but always undergo more or less decomposition when heated above 250° C. In the vacuum of the cathode light, however, it has been found possible to effect distillation without decomposition. Oils and fats refract light in varying degrees; advantage is taken of this property in analysis.

The optical activity (power to rotate a beam of polarised light) is but slight for the majority of fats. The cholesterol or phytosterol derivatives present in the oil are chiefly responsible for this slight optical activity.

The fats are practically insoluble in water; most oils and fats are, however, capable of dissolving minute traces of water. In the presence of small quantities of soap, albumen, etc., the oils can form exceedingly stable emulsions with water.

Ether, petroleum spirit, benzol, carbon bisulphide, and the chlorinated hydrocarbons dissolve oils and fats with great readiness (with the exception of castor), but cold alcohol only sparingly dissolves them.

In hot alcohol, or if large quantities of free fatty acids are present, they are freely soluble. It is particularly interesting to notice that the solubility of a glyceride in any menstruum is enormously affected by the presence of either other glycerides, free fatty acids or unsaponifiable matter; thus, 100 parts of ether only dissolve ·5 parts of pure tristearin at 20° C., but if the stearin be mixed with 5 per cent. of triolein, twelve parts of the mixture are soluble. Also if the free fatty acids represent more than 30 per cent of an oil, it is generally soluble in cold alcohol. The fats are capable of dissolving halogens, sulphur and essential oils or perfumes (enfleurage).

Influence of Physical and Chemical Agents and Chemical Changes of the Fats and Oils.

The chief physical agents with which we are concerned are (*a*) heat, and (*b*) light.

Pure non-drying oils and fats may be heated to 200° C. for a

considerable time without appreciable change taking place provided air is excluded, but when heated above 300° C. all oils begin to decompose, with the formation of pungent vapours. The aldehyde acrolein $CH_2{=}CH.CHO$ invariably is produced by this decomposition, and its penetrating odour is typical of heated fatty oil. Prolonged heating at temperatures of 250 to 300° C, in the case of castor and oils containing unsaturated glycerides (tung oil, linseed oil, liver oils, etc.), results in the formation of either thick viscous, gelatinous or even solid products. This result, which is made use of in the arts (oil boiling), is probably attained by the combined influence of oxidation and polymerisation. If a current of air be blown through some of the oils heated to this temperature the viscosity of the material is enormously raised, and a "thickened" oil produced.

When exposed to the air in thin films, oils containing highly unsaturated glycerides absorb oxygen, forming hard films insoluble in most organic reagents (drying oils). In order to secure complete drying, glycerides containing at least two double bonds in the molecule appear to be necessary, and the marked siccative property of linseed oil has been attributed largely to the presence of glycerides of linolenic acid which possesses three unsaturated linkages.

The time required by an oil to "dry" is greatly influenced by previously heating the oil in contact with air and oxidising agents (oil boiling). Whether the process of oxidation and polymerisation of oils is influenced by light is not known with absolute certainty, but undoubtedly light is an active agent in destroying certain colour stuffs present in the oil. Thus linseed, olive, and medicinal cod liver oils are occasionally bleached by exposure in thin layers to sunlight.

When an oil is exposed to the action of air and light for some time it frequently happens that it develops an unpleasant odour and taste and is then said to have become "rancid." It is impossible at the present time to define rancidity chemically within any degree of accuracy, and one relies in the main simply on the senses of taste and smell to detect the change.

Formerly it was thought that rancidity was due chiefly to the breaking down of the glycerides into free fatty acids. This is,

however, by no means the case, since a fat may become rancid without marked rise in the percentage of free acids, and further, acid fats are not necessarily rancid. In fact a certain amount of free acids in edible oils, such as olive and arachis, imparts a pleasant and distinctive flavour. The peculiar unpleasant odour of rancid oil appears to be due to the presence of minute amounts of decomposition products of the glycerides, chief of which are lower fatty acids, such as acetic, butyric, caproic, and their esters, dibasic acids, aldehydes and ketones, all of which have been detected in rancid fats. The cause of rancidity appears to be due to the combined influences of moisture, oxygen, ferments, enzymes, and probably bacteria.

Influence of Reagents.

Nitrous Acid has no action on the saturated glycerides, but olein is converted by it rapidly into its isomer elaidin. Linolic and the more highly unsaturated glycerides are but little affected.

Nitric Acid: in the cold, oils containing saturated glycerides in preponderating quantities are practically unaffected, but when treated with hot acid, oxidation takes place with a breaking down of the glyceride into acids and glycerol.

Warm nitric acid oxidises the unsaturated oils forming *OH* groups at the double bonds. By continued action nitro bodies are formed, those from linseed and castor being thick masses used as caoutchouc substitutes (nitrated oils).

Sulphuric Acid:—in the cold, concentrated H_2SO_4 attacks the unsaturated linkages, forming sulphonated oils. Geitel isolated a sulpho-glyceride of formula

$$C_3H_5\begin{cases}OC_{18}H_{33}O\\OC_{18}H_{34}SO_4OH\\OC_{18}H_{34}OH.O\end{cases}$$

from the reaction products of sulphuric acid on olive oil.

The reaction will be more fully considered under Saponification of Glycerides.

Hydrolytic Agents.—Alkalis, steam, etc., decompose the glycerides into acids and glycerol.

Halogens.—Chlorine, bromine and iodine in the hot substitute an atom of hydrogen in the saturated glycerides, but are rapidly absorbed by unsaturated oils with the formation of addition compounds.

Sulphur.—When the saturated glycerides are heated to 250° C. with sulphur, H_2S is evolved and substitution takes place. The unsaturated oils absorb sulphur at 150° C.

S_2Cl_2 adds at the double bonds, giving in some cases solid products (vulcanised oils).

The compound with oleic acid appears to be formed from two molecules of the acid joined by sulphur, thus:—

$$\begin{array}{l} CH_3.(CH_2)_7.CH-CH-(CH_2)_7.COOH \\ \qquad\qquad\quad |\qquad\ |\ \\ \qquad\qquad\quad S\quad Cl \\ \qquad\qquad\quad | \\ \qquad\qquad\quad S\quad Cl \\ \qquad\qquad\quad |\qquad\ | \\ CH_3.(CH_2)_7CH\ .\ CH.(CH_2)_7.COOH \end{array}$$

CHAPTER VI

COMPOSITION AND PROPERTIES OF THE INDIVIDUAL OILS AND FATS OF COMMERCIAL IMPORTANCE

It is convenient to classify the natural oils and fats according to their source into

(1) vegetable, and (2) animal oils and fats.

Such a division is not marked by any great differences in chemical composition of the saponifiable constituents of either group, but when we turn to the unsaponifiable matter contained in every natural oil or fat the difference is well defined, since all animal fats contain the alcohol cholesterol, while those of vegetable origin are distinguished by the presence of phytosterol. The animal oils and fats may be further sub-divided into those obtained from (*a*) terrestrial, (*b*) marine animals or fishes. The former are characterised by relatively small iodine values, and with the exception of neatsfoot all those of commercial importance are more or less solid fats at ordinary temperatures prevailing in this country. The marine animal oils on the contrary are, with few exceptions, limpid liquids containing large quantities of highly unsaturated acids of complex composition.

By far the largest quantities of oils and fats are obtained from the seeds and fruit of plants, and it is customary to classify them according to their iodine value and the composition of their glycerides into four groups, viz.:—

(1) Solid fats;

(2) Non-drying oils;

(3) Semi-drying oils;

(4) Drying oils.

This system of classification, although convenient for the purposes of study, is in no sense absolute, since oils and fats are known which stand on the boundary between each group and

which might easily be classed among the fats or non-drying, semi-drying or drying oils, as the case may be.

Vegetable Fats and Oils.

The vegetable fats and butters form a natural group of fats with melting points ranging from 21° to 43° C. (Japan wax melting at 48° to 53° C. is exceptional in this respect), and consequently vary from a buttery consistency to a hard crystalline mass.

The specific gravities also vary widely from ·915 to ·950 at 15° C. Since they contain but small amounts of liquid acids they are characterised by relatively low iodine figures and rarely absorb more than 50 per cent. of iodine, while in the case of coconut the iodine value falls as low as 9 per cent. All form excellent soap-making material, and many find application in the candle and edible fat industries.

The more important representatives of the group are coconut, palm, and palm kernel oils. Shea butter, cocoa butter, Japan wax, and Chinese vegetable tallow are also found upon the market, but in relatively less quantity, although more extended exploitation of the tropics will no doubt rapidly increase the quantities of these products imported.

The *non-drying oils* are liquid; they are characterised by possessing preponderating quantities of olein and rarely absorb more than 95 per cent. of iodine.

Their specific gravities range from ·915 to ·925. When cooled most of them deposit "stearine," which when filtered off leaves an oil which does not congeal at 0° C.

The best-known non-drying oils are olive, olive kernel, arachis or earthnut, and castor oils.

The *semi-drying oils* are so called because they lie intermediate in their composition and properties between the non-drying and the drying. When exposed to the air in thin films for a long time they absorb some oxygen and become sticky, due no doubt to their content of linolic glycerides. They absorb from 100 to 120 per cent. of iodine and fall within the limits of ·913 and ·925 of specific gravity at 15° C. The oils of this class which find industrial application are cottonseed, sesamé, soya bean and rape oils.

The *drying oils* absorb over 120 per cent. of iodine, and when exposed to the air in films for a few days oxidise and polymerise, forming more or less hard and elastic films. Since they contain such highly unsaturated molecules they are very reactive chemically, a property which is employed for a variety of purposes.

Most members of this group remain liquid when cooled far below zero. They are in general specifically heavier than the non-drying and semi-drying oils, varying from ·925 to ·935 at 15° C.

Only two are of great commercial importance, viz., linseed and tung oil; but sunflower and poppyseed oil would seem to have an industrial future.

Terrestrial Animal Fats.—The fats which fall into this class vary like the vegetable fats from butters melting at about 30° C. to hard tallows, which do not liquefy until a temperature of 42° to 43° C. is reached. Containing large quantities of saturated glycerides, their iodine value is generally below 55 per cent. and rarely exceeds 80 per cent.

The composition, and therefore the analytical figures for any particular fat, varies within fairly wide limits according to the age and food of the animal from which the sample has been obtained. The specific gravity at 15° C. varies from ·915 to ·950. Four only are of importance, viz., lard, tallow, bone and butter fat.

The *marine animal* oils form a very definite group characterised by high iodine absorption (from 110 to 160 per cent.) due to the large quantity of highly unsaturated acids which they contain. They are further sub-divided by Lewkowitsch into

(*a*) Fish oils;
(*b*) Liver oils;
(*c*) Blubber oils;

according to the particular part of the fish from which they are obtained.

All are liquid oils, but the fish and blubber oils deposit "stearine," or waxes, when cooled.

The specific gravities range from ·915 to ·940.

In the following pages a brief survey will be made of those oils and fats which are of great commercial importance.

For detailed descriptions of these and other oils reference must

be made to the larger treatises of Ubbelohde, Lewkowitsch, etc. (see Bibliography).

For convenience we will consider them under the headings of (*a*) vegetable fats; (*b*) vegetable oils; (*c*) animal fats; (*d*) animal oils.

VEGETABLE FATS.

Palm Oil is obtained from the fruit of the oil palm (Elæis Guineensis), vast forests of which flourish on the west coast of Africa.

On this coast the preparation of oil from the outer portion of the fruit of the palm constitutes a great industry. The usual method of preparation employed is to throw the fruit into a hole dug into the ground, sprinkle it with water, and then (after covering with leaves and stones) the mass is allowed to stand for some days. By this means the fleshy part of the fruit becomes softened and the inner kernel (palm kernel) can be easily removed. The fleshy fruit is then pounded into a pulp, mixed with water, and well boiled until the oil rises to the surface, when it is skimmed off and packed in barrels for shipment. This rough method of preparation gives a product highly contaminated with dirt, decayed leaves, etc., which tend to allow the oil to decompose and become rancid upon standing.

Recently, however, attempts have been made to import the fruit into Europe and express the oil by pressure.

Palm oil varies from a light yellow to a dark red colour, and is of a buttery or tallow-like consistency, according to the district from which it comes. Three classes of palm oil are commercially recognised:

(1) Soft oil, from Lagos, Calabar, and Bonny.

(2) Hard oils, from the Congo, Niger, and Gold Coast.

(3) Mixed oils, generally from the Gold Coast district.

In the fresh state it contains about 10 to 15 per cent. of free fatty acids, but on long standing decomposes almost entirely into glycerine and fatty acids. The fatty acids contained in palm oil are chiefly palmitic and oleic. The chemical and physical constants vary considerably with the locality of the oil. They are, however, on the average:–

CHEMICAL AND PHYSICAL CONSTANTS[1] OF PALM OIL.

Specific gravity.	Melting point.	Solidifying point.	Saponification value.	Iodine value.
0·921/0·924 at 15° C.	From 27 to 42·5, according to the age and origin of the oil.	30° C. to 40° C.	197/203	52/55

CHEMICAL AND PHYSICAL CONSTANTS[1] OF THE INSOLUBLE FATTY ACIDS.

Hehner value.	Specific gravity.	Solidifying point.	Neutralisation value.	Iodine value.
96 per cent.	·8369 at 99° C., water at 15·5° C.=1°	44·13° C.	206 milligrammes *KOH*	53·3

Palm oils from different sources show varying behaviour towards bleaching agents: *e.g.*, Lagos and Calabar oils bleach fairly easily by blowing with air in the hot or washing with bichromate, while Congo oil is bleached only with great difficulty. The fine white products obtained by successful bleaching are of great value to the soap and candle maker.

Palm Kernel Oil.—Palm kernel oil is obtained from the kernels of the palm tree fruit, the outer flesh of which, as we have seen, is a source of palm oil. The kernels, which are imported in great quantity into Europe, yield from 40 to 45 per cent. of oil by expression.

It is a white fat with a characteristic smell and nut-like flavour, and contains appreciable quantities of lower fatty acids. Its chemical composition has not been fully worked out, but the chief

[1] NOTE.—The methods of determining and interpreting the "constants" are explained in Chapter VIII.

constituent seems to be lauric acid. Its physical and chemical factors are:—

CHEMICAL AND PHYSICAL CONSTANTS OF PALM KERNEL OIL.

Specific gravity.	Melting point.	Solidifying point.	Saponification value.	Iodine value.	Reichert-Meissl value.
·925 at 15° C.	23/28° C.	23° C.	242/250	13/14	5/7

PHYSICAL AND CHEMICAL CONSTANTS OF THE INSOLUBLE FATTY ACIDS.

Titer.	Melting point.	Neutralisation value.	Hehner value.	Iodine value.
20/25	25/28·5° C.	258/265	91·1	12

Palm kernel oil finds great demand in the soap industry and in the manufacture of vegetable butters.

Coconut Oil.—Coconut oil is a solid fat obtained from the kernel of the coconut, which flourishes in various parts of the tropics, where it is prepared by the natives in a similar manner to that described for palm oil. In commerce three qualities of oil are recognised:—

(1) Cochin. (2) Ceylon. (3) Copra.

The former is a very pure variety of an excellent white colour and containing only a small percentage of free fatty acids. Ceylon oil contains a much higher percentage of free fatty acids, no doubt owing to the careless method of preparation practised by the natives. Quantities of the dried kernels are imported into Europe, known as copra. On expressing the dried kernels in the hot, about 63 to 66 per cent. of oil is obtained.

Stearic, palmitic, oleic, myristic, and lauric acids as triglycerides have been detected in coconut oil, but in addition it contains small quantities of lower acids, butyric, caproic, etc., which accounts for the high Reichert-Meissl figure which coconut oil always shows.

The more important physical and chemical characteristics of coconut oil are set out in the table :—

CHEMICAL AND PHYSICAL CONSTANTS OF COCONUT OIL.

Specific gravity 15·5° C.	Melting point.	Saponification value.	Iodine value.	Reichert-Meissl value.
·925/·926	23/26° C.	253·4 to 262	8 per cent. to 9 per cent.	7 to 8

The insoluble fatty acids have a mean molecular weight of 200 and titer test 21 to 25.

Coconut oil enters largely into the composition of vegetable butters and margarines. The Ceylon oil is used in soap and candle making.

It is interesting to note that coconut possesses the highest saponification and lowest iodine value of all fats or oils.

NON-DRYING OILS.

Vegetable Oils.

Olive Oil.—Olive oil is obtained from the fleshy part of the fruit of the olive tree, which contains from 40 to 60 per cent. of oil. The olive flourishes in Italy, Spain and the south of Europe. The oil is obtained from the fruit on the spot by a crude method of expression, generally by hand power. The best qualities of oil are obtained from the fresh fruit, and find a ready sale as edible oils, while an inferior quality is obtained by allowing the fruit to ferment before extracting. Oil of this class contains large quantities of free fatty acids, and finds its chief use in the manufacture of soap. After two or three extractions there remains a pulp containing from 10 to 20 per cent. of oil, which is further removed by treatment with bisulphide of carbon. This reagent removes at the same time the green colour stuff chlorophyll which imparts to the oil a dark green hue. This extracted oil, which is fairly rich in solid glycerides and contains some sulphur from the solvents, is known in commerce as sulphur oil. Olive oil varies from a pale yellow to a darkish green, and

has a characteristic odour and smell. The oil contains about 28 per cent. of solid glycerides, chief of which is palmitin, and about 70 per cent. of liquid glycerides almost wholly composed of oleic acid. The physical and chemical constants of olive oil are :—

Specific gravity. at 15° C.	Solidifying point.	Saponification value.	Iodine value.
·915/·918	Various. Stearine separates about + 5° C.	about 190	generally 82

The fatty acids generally melt at about 24° C., and solidify from 18 to 27° C.

In addition to its employment as an edible oil, olive oil finds application for a variety of purposes, such as burning oil, lubricating oil, and textile oil. Its adulterants may be cotton-seed oil, arachis and sesamé oils.

Arachis or Nut Oil.—An oil of great importance is obtained from the seeds of the arachis plant which grows in abundance in Brazil, West Africa and the Levant.

The seeds (which are commonly called "earth nuts") consist of a hard shell enclosing a kernel, from which the oil is extracted. The decorticated kernels yield from 35 to 40 per cent. of oil on pressing. Since the nuts are rich in oil it is advisable to press them three or four times in order to obtain the most satisfactory results.

The oil which exudes in pressing at ordinary temperatures (cold drawn) is a pale limpid liquid of pleasant taste, and finds a market for the manufacture of edible oils.

When as much oil as possible has been drawn in the cold, the cake is heated to about 100° F. and again pressed for the preparation of seconds oil. A further 8 to 10 per cent. of oil may be extracted by a third pressing at 150 to 160° F. The residual press cake, containing a few per cents. of oil, forms an excellent cattle food.

Second-pressure oil is usually of good colour and, after

filtration through earth or charcoal, is employed for edible purposes; but if prepared from old seeds, it is sold to the soap-makers.

The third-pressure oil which contains a considerable amount of impurities of a non-fatty nature, dissolved out of the cake by the hot oil, is used exclusively for soap-making.

When chilled, arachis oil deposits a "stearine" which may be separated to some extent by decantation, but its complete removal by filtration is exceedingly difficult, owing to the gelatinous nature of the precipitate which tends to pass through the cloth. The solid "stearine" consists chiefly of the glyceride of arachidic acid $C_{19}H_{39}COOH$.

Arachis oil contains the glycerides of arachidic, lignoceric, palmitic, oleic and linolic acids. The unsaturated acid hypogaec has been detected in the oil by Gossmann and Schröder.

The best quality oils contain less than 1·0 per cent. of free fatty acids.

Arachis oil may readily be detected in admixture with other oils by isolating arachidic acid identified by its melting point (72 to 74° C.). The saponified oil is converted into lead soaps and extracted with ether. The lead salts of the liquid acids are thereby removed, and from the insoluble residue arachidic acid can be obtained and purified by crystallisation from alcohol.

Arachis oil shows the following average constants:—

Specific gravity at 15° C.	Solidifying point.	Saponification value.	Iodine value.	Hehner value.
·917 to ·919	+2 to 0° C.	189—193	90—100 per cent.	94·8—95·8

The insoluble fatty acids solidify at 28·1 to 29·2° C., and have a mean molecular weight of 282.

Castor Oil is obtained from the seeds of the castor plant (*Ricinus Communis*) which grows abundantly in India, Mexico, and the United States of America, from which countries the bean is exported to England and France.

The kernels, which contain over 60 per cent. of oil, are surrounded by a mottled husk which is generally removed before proceeding to extract the oil.

It is usual to press the meal in the first place at ordinary temperatures, when about 30 per cent. of a pale oil of great purity is obtained.

This oil, known as first-pressure castor, is used to some extent in medicine, and since it contains very little free fatty acids is largely employed as a lubricating oil. The cake is then removed and again pressed when about 10 per cent. of dark-coloured oil (seconds) is obtained. The residue, still retaining as much as 8 per cent. of oil, may be extracted with solvents and the meal then used as manure.

The castor bean contains a very poisonous alkaloid (ricine) which is found in the hot pressed and extracted oils, and also in the cake, which is thereby rendered totally unfit for feeding purposes.

The seed also contains a powerful hydrolysing enzyme.

The expressed oil requires practically no further treatment beyond heating to coagulate the albumins and destroy the activity of the enzyme.

Castor oil varies in colour from light yellow to dark brown, and possesses a characteristic smell and taste.

It is readily distinguished from other oils by its high viscosity and solubility in cold alcohol and glacial acetic. It is only miscible with petroleum ether in certain proportions, but on heating to 300 to 400° C. for a short time under pressure, it polymerises and becomes miscible in all proportions. Its most important constituents are the glycerides of ricinoleic and dihydroxystearic acids, to which its high acetyl value and peculiar solubility relations are due.

It reacts with concentrated sulphuric acid, forming a sulphonated oil.

Castor oil is used in medicine, as a lubricant, for the manufacture of Turkey red oil, and to a limited extent in the soap industry.

The average chemical and physical constants of castor oil are:—

Specific gravity at 15° C.	Solidifying point	Saponification value.	Iodine value.	Reichert-Meissl value.	Acetyl. value.	Viscosity.
·960/·966	−10 to −12° C.	180/185 milligrammes *KOH*	83 to 90·6 per cent.	1·1	149·9 to 150·5	In seconds (Redwood) 1160 to 1190 at 100° F.

SEMI-DRYING OILS.

Cotton-Seed Oil. The seeds of the cotton plant, which flourishes in the United States of America, Brazil, South America, India and Egypt, yield from 20 to 22 per cent. of oil.[1]

The kernel is covered with a husk to which the well-known cotton fibre adheres. American crushers generally remove this husk in specially constructed machines before proceeding to extract the oil, but Egyptian, Indian and Levantine seeds are generally crushed in England in an undecorticated state.

The crude oil, as it flows from the press, has a red to blackish colour, due to the presence of quantities of colour stuff present in the cells, which is expressed with the oil.

The intensity of this colour varies greatly with the age of the seeds, and hence American oils, which are obtained from fresh seeds crushed on the spot, are of a much paler colour than English oils. The press cake, which contains from 5 to 10 per cent. of oil, forms an excellent food for cattle. Cotton-seed oil is refined by treating it with dilute caustic lyes at about 50° C.

The quantity of alkali added should be just enough to combine with the free fatty acids and colouring matter, but insufficient to cause saponification. This percentage of alkali is usually ascertained by a small experiment in the laboratory, and is adjusted until, on allowing the mixture of oil and lyes to stand, it rapidly separates into two layers. If too much or too concentrated a solution of caustic is employed persistent emulsions form, which are most difficult to separate. After treatment, the alkaline liquors are withdrawn (foots), and the supernatent oil washed with water until free from alkali.

On allowing to stand in the warm to clarify, a pale yellow oil, containing not more than 1 per cent. of free fatty acid, is obtained.

[1] Calculated on the whole seed.

The foots, which consist of a soap solution mixed with mucilage and colour stuff, are generally treated with mineral acid, and washed with warm water, preparatory to being subjected to distillation in a current of steam, for the preparations of oleines and stearines. The refined oil is sometimes bleached with bleaching powder. Cotton-seed oil when cooled below 20° C. deposits a stearine, which is sometimes separated and sold as cotton-seed stearine, for the manufacture of lard and butter substitutes. The oil freed from stearine remains fluid and clear at the temperature of freezing point, and is known as "winter oil," or demargarinated cotton-seed oil. Cotton-seed oil appears to consist chiefly of the glycerides of palmitic, oleic and linolic acids, and Lewkowitsch "considers it doubtful whether stearic acid is present." The physical and chemical constants are as follows:—

Specific gravity at 15° C.	Solidifying point.	Sapon'fication value.	Iodine value.
·922/·930	3/4 Stearine separates out at 10/12	191/196·5	106/120

Characteristics of the insoluble fatty acids:—

Specific gravity.	Solidifying point, Titer.	Neutralisation value.	Iodine value.	Hehner value.
·920/·922	33/37·6 Winter oil 28·1/28·5	201·6/208	110/115	96

Cotton-seed oil is used for edible purposes and for the manufacture of soap.

Sesamé Oil.—The seeds of *Sesamum Indicum*, which are produced in India, China, Japan and the Levant, are exceptionally rich in oil, and frequently contain as much as 50 to 57 per cent. When good fresh seeds are used the oil is most satisfactorily obtained by pressing, which process must be conducted in several

stages, owing to the high content of oil in the meal. The yield of oil on an industrial scale is from 42 to 48 per cent., and the press cake, which retains about 10 per cent. of oil, is a perfect feeding stuff; but if the seeds are damaged and the press cake which they would yield, therefore, unfit for food, it is customary to extract the oil from the meal with carbon bisulphide.

Raw sesamé oil is light coloured and fairly rich in "stearines," which are deposited on allowing the oil to stand in the cold.

The oil frequently contains large quantities of free acids which must be removed if it be intended for use as an illuminant.

The fatty acids of sesamé oil appear to consist of a mixture of about 78 per cent. of liquid acids (oleic and linolic) and 12 to 15 per cent. of solid acids (stearic, etc.).

Sesamé oil may readily be detected in mixtures by the Badouin reaction,[1] and for this reason the German law requires margarine makers to incorporate a certain proportion of the oil into their products to facilitate detection of adulteration of butter with margarine.

Sesamé oil is of great value to the soap-maker, but the better qualities are used in the edible oil and fat industries.

ANALYTICAL FACTORS OF SESAMÉ OIL.

Specific gravity at 15° C.	Solidifying point.	Saponification value.	Iodine value.	Reichert-Meissl value.
·923	4 to 6° C.	188·5 to 190·4	106·9 to 107·8	1·2

CHEMICAL AND PHYSICAL CONSTANTS OF THE INSOLUBLE FATTY ACIDS.

Hehner value.	Solidifying point.	Iodine value.	Mean molecular weight.
95·8 per cent.	20/25° C.	111·8 to 112·0	286

[1] See p. 131.

Soya Bean Oil.—The soya bean contains about 18 per cent. of oil and 30 to 40 per cent. of protein. It is grown in great quantities in Manchuria, China and Japan, where the extraction of the oil forms a most important industry. The Manchurians prepare the oil by soaking the beans in water, crushing them, and then extracting in a press. In Europe considerable success has attended the preparation of this oil by expression or extraction by solvents, which yields a reddish coloured oil, with a characteristic odour.

Soya bean oil, although only introduced upon the European market comparatively recently, has found wide and varied application in the manufacture of boiled oils and soap. It contains about 80 per cent. of the glycerides of liquid fatty acids, the bulk of which are oleic and linolic, while the solid acids appear to be palmitic.

Comparatively few analyses of this oil have been published. The following table gives the physical and chemical constants of the oil :—

Specific gravity at 15° C.	Solidifying point.	Saponification value.	Iodine value.
·924/·927	8/15° C.	190·6/192·9	121·3/125·2

The insoluble fatty acids melt at about 28° C., solidify at 25° C. and have an iodine value of 115·2 to 122.

Rape (Colza) Oil.—The rape seed is grown in East India, Argentine and Europe, and contains from 35 to 45 per cent. of oil, which is obtained from it either by expression or extraction.

When the expression process is employed with rape seed a large amount of mucilage is brought out with the oil, which must be removed before the product is marketable.

The extracted oil is purer; but on the other hand, while the press cake is an excellent cattle food, the extracted meal is only of use as a manure.

The dark crude oil is always refined by Thenard's process, which consists in agitating the oil with 1 per cent. of its weight

of conc. H_2SO_4 which coagulates the albuminous impurities and precipitates the colour stuffs.

The refined oil is pale yellow in colour and possesses a typical smell. It is known in commerce as either rape or colza.

The chief components of rape oil are the glycerides of the unsaturated rapic and erucic acids mixed with a little stearic arachidic and linolic acids.

On standing in the cold some "stearine" usually separates out.

Next to castor, rape possesses the highest viscosity of any fatty oil, and is frequently adopted as a standard in commercial viscometry.

Rape oil finds extensive application for burning and lubricating, for which purposes it should not contain more than 8 or 9 per cent. of free fatty acids.

When rape oil is heated and a current of air blown through the hot oil oxygen is rapidly absorbed, the specific gravity rises and the iodine value falls. The reaction, which is apparently one of oxidation and polymerisation, is accompanied by an enormous rise in the viscosity. The viscous product is placed upon the market for lubricating purposes as blown or thickened rape oil.

The analytical factors of rape oil are :—

Specific gravity at 15° C.	Solidifying point, °C.	Saponification value, milligrammes. *KOH.*	Iodine value, per cent.	Reichert-Meissl.	Viscosity at 60° F. (Redwood).
·914/·917	10/ summer variety 10/ winter variety	171·7 to 176·5	98·/103·6	·3/·79	525 to 540 seconds

DRYING OILS.

Linseed Oil.—Obtained from the seeds of the flax plant, which flourishes in India, Russia, Argentine, and the United States of

America chiefly. The imports of linseed into Great Britain are very extensive, and the expression of linseed oil from the seed constitutes a big industry.

On the market linseed is known in various qualities according to its source, the more general being Baltic oil and Black Sea oil (two types of Russian products), East India oil and River Plate oil. Baltic linseed yields the best and purest drying oil, but Black Sea seeds generally contain a few per cents. of foreign seeds (hemp or ravison), while Indian seed invariably contains small quantities of mustard and rape seeds.

The oils obtained from the above-mentioned brands of seeds vary somewhat in degree of purity, a point which must not be lost sight of when studying the composition of linseed oil.

Linseed from all sources is prepared by a process of expression, since the press cake is a most valuable feeding stuff. For the preparation of paint oils, the crude linseed requires to be refined by treating it with 1 or 2 per cent. of its weight of concentrated sulphuric acid, which acts as explained on p. 79. The oil thus refined varies in colour from yellow to very light orange, and if it be intended to employ the oil in the manufacture of the finest paints (artists' colours, etc.), it is bleached by mixing it with powdered lead, and exposing it in shallow dishes to the action of sunlight. In the soap industry, excessive quantities of colour stuff may be removed from the oil by a preliminary refinement with caustic alkalies. The above remarks apply to warm expressed oil; by cold expression a light yellow oil may be obtained which is used as an edible oil.

Linseed oil is, par excellence, the drying oil for paint and varnish making, in which industries it is employed in both the raw and boiled state. The process of boiling and the composition and properties of the boiled oil is discussed on p. 161.

The composition of linseed oil is somewhat complex. It owes its drying properties mainly to the presence of the glycerides of linolenic and isolinolenic acids, which constitute 60 to 70 per cent. of the oil. On allowing to stand in the air for some time, small quantities of oxidised acids are produced by a process of oxidation and polymerisation. If properly refined the oil, when heated for a few moments to 200° C., should remain clear on cooling, and no mucilaginous matter be deposited.

PHYSICAL AND CHEMICAL PROPERTIES OF LINSEED OIL.

Specific gravity at 15° C.	Saponification value.	Iodine value.	Acid value.	Hexo-bromide.
·932/·937	190/195	170·1/194·3	Various. Generally below 7.	23·8 to 25·6

Besides its employment in the paint and varnish industries, linseed oil finds extensive application in the manufacture of soft soap.

ANIMAL FATS.

Tallow.—Two kinds of tallow are recognised in commerce, namely, beef tallow from oxen, and mutton tallow from sheep and goats.

The fat is rendered from the rough tissue at a temperature of about 100° C., unless it be intended for use in the manufacture of oleo margarine, in which case the best quality of raw fat (suet) is selected and rendered at a temperature between 40 and 50° C. The fat prepared in the latter way is known as "Premier Jus," and is further worked up into beef stearine (or mutton stearine) and oleo oil. The premier jus is cooled to 25° C., and subjected to pressure, when hard stearine is obtained and a buttery oil exudes from the press. The latter is called oleo-oil or oleo-margarine, and is used in the manufacture of butter substitutes.

By pressing the rendered tallow at the ordinary temperatures (cold), a small quantity of oil is obtained known as tallow oil, hence we have five distinct commercial products :—

(1) Rendered tallow, which is a mixture of all the fat in the carcase.
(2) Premier Jus.
(3) Tallow stearines, obtained by warm pressing (1).
(4) Oleo oil, or oleo margarine, a by-product in the manufacture of (3).
(5) Tallow oil, obtained by the cold pressing of (1).

Tallow is valued according to its colour, odour, and hardness

the latter being expressed in terms of the solidifying point of its fatty acids (tallow titer).

The quality of a tallow depends on the food, breed, and age of the animal.

Tallow consists essentially of a mixture of glycerides, of stearic, palmitic and oleic acids, the relative proportions of which vary according to the age, foodstuff, and breed of the animal; in general, mutton tallow is harder, and possesses a higher titer than beef tallow. In the following table the physical and chemical constants of beef and mutton tallow are compared.

	Specific gravity at 15° C.	Melting point.	Saponification value.	Iodine value.
Beef . .	·943/·952	46/48° C.	193/198	40/47·5
Mutton .	·937/·953	47/49° C.	192/195	35·2/46·2

Properties of the insoluble fatty acids :—

	Solidifying point, Titer.	Neutralisation value, milligrammes *KOH.*	Iodine value.	Hehner value.
Beef . .	43·5/45	197·2/201·6	41/48	95·5/96
Mutton .	44/46	210	35/46	95·5/

Lard.—The term "lard" was originally applied to the leaf fat from the kidneys and bowels of the hog, which was rendered in small establishments and packed in bladders; hence the name, "Bladder Lard."

Nowadays the growth of the large slaughter-houses of America has resulted in the manufacture of lard from the fat of all parts of the hog.

Five qualities of commercial lard are recognised, viz. :—

(1) Neutral No. 1.

(2) Neutral No. 2.
(3) Leaf.
(4) Choice.
(5) Prime steam refined.

Immediately the animal is killed, the kidney and bowel fat is placed in steam jacketed kettles and heated to about 45° C., when a fine quality of fat, consisting exclusively of glycerides, is obtained, known as Neutral No. 1.

The "back" fat is similarly treated, when imitation neutral or Neutral No. 2 is obtained.

The residue from the extraction of Neutrals still contains a quantity of fat, which is removed by subjecting it to the action of high pressure steam in autoclaves. The product so obtained, called leaf lard, is very pure and keeps well. Prime steam lard is prepared by steaming under pressure from the mixed fatty tissues from all parts of the hog.

The guts, feet, etc., are sometimes autoclaved separately for the preparation of yellow grease used in soapmaking.

The neutrals need practically no refining, being always of a high degree of purity when obtained from fresh tissue, and they find application almost exclusively in the preparation of margarines.

The commoner grades of leaf and steam are mixed with earth and blown with air to bleach and deodorise. The material is then filtered and the molten fat run into troughs in which cylinders chilled with ice water rotate. (Lard Coolers.) The rotating cylinders congeal the layers of fat in contact with them, which is then carried up by the roller and scraped off at the top. This is done to make the stearine crystallise out in small grains throughout the mass, and so give the characteristic salve-like consistency.

The composition and hardness of the lard depends largely on the food of the pig.

Lard appears to consist of the glycerides of lauric, myristic, palmitic and stearic acids with from 50 to 60 per cent. of oleic and a trace of linolic. It always contains about ·2 per cent. of cholesterol.

Its adulterants are generally beef and cotton-seed stearines

which may be detected by the usual tests, supplemented by observing the crystals formed by slowly evaporating an ethereal solution.

These crystals, when examined by the microscope, show fairly definite forms.

When prime steam lard is slowly cooled from the molten state crystals of stearine form, and may be separated by pressure, yielding lard stearine and lard oil.

The former is used for stiffening soft lards and magarines; the latter, being practically neutral, is used as a burning and lubricating oil.

Physical and Chemical Constants of Lard.

Specific gravity at 15° C.	Melting point.	Solidifying point.	Saponification value.	Iodine value.
·934/·938	36/45° C.	27·1 to 29·9° C.	195·2 to 196·6	50 to 70 per cent.

The fatty acids form 95·5 per cent. of the lard, solidify at 36/42° C., and have a mean molecular of 278.

Bone Fat.—Good fresh bones contain from 12 to 20 per cent. of fat. The fat is extracted either by boiling the disintegrated bones with water and separating the supernatent fatty layer from the glue solution, or by digestion with pressure steam in autoclaves. For many purposes, however, it is preferable to remove the fat by extracting the bones with solvents, and this process is now almost universally employed.

The solvent used exclusively is petroleum naphtha, boiling between 100 and 150° C. which obviates the necessity for drying the bones as explained in Chapter III.

The fat obtained from fresh material varies from white to yellow and is of good odour, but when old bones which have been allowed to undergo decomposition are used, a dark coloured product is obtained highly charged with volatile acids, lactic acid (by fermentation), and lime soaps, formed by the action of the free acids on the lime of the bone.

Such a fat can only be bleached with difficulty; products of good colour may be obtained by treatment of the crude fat with bichromate solutions, but it is found that, after bleaching, the colour returns to some extent in a few days.

It is important to note that the more free fatty acids it contains the more difficult it is to satisfactorily bleach bone fat.

The better qualities of bone fat, particularly those obtained by steam extraction, are good enough for soap-making, but the benzine-extracted products and poorer qualities usually find a market for grease-making, and, after saponification and distillation, for the manufacture of candles.

Bone fat consists essentially of the glycerides of stearic and oleic acids. It is valued in commerce according to the content of non-fatty impurities, water, etc., and also upon its "titer."

ANALYTICAL CHARACTERISTICS OF BONE FAT.

Specific gravity at 15·5° C.	Melting point.	Saponification value.	Iodine value.	Unsaponifiable matter.
·914/·916	20/22° C.	190/194	46/49 per cent.	1/2 per cent.

The fatty acids solidify at about 30° C.

Fish Oils.

The oils comprised in this class are obtained from the body fat of fish. The yield of oil is very poor, and the industry is carried on largely for the preparation of the other fish products (glue, fish-scrap, manure, etc.).

The oils are obtained by boiling the fish with live steam in false-bottomed tanks. The flesh rapidly disintegrates, and the oil, rising to the surface, is skimmed off. It is important to obtain the fish as fresh as possible because the oil from putrid material is always highly charged with impurities which are impossible to remove on a commercial basis.

The fresh fish are boiled with water and the oil separated off as quickly as possible, prolonged boiling in contact with the

"fishy" mass exerting an injurious effect on the purity of the oil.

The product of the first boil where due precautions have been taken is fairly pale in colour and needs but little refining. The residue in the vat still contains oil which is best extracted by packing it into bags and pressing, when a dark oil is obtained.

The fish oils invariably contain some solid "stearine" which separates out in the cold. The solid matter may be pressed to separate it from adhering liquid oil, and sold as fish tallow cake.

The process of refining usually consists in demargarinating and then filtering the clear oil through charcoal to bleach. Occasionally a treatment with concentrated soda lyes to remove free fatty acid and improve the colour is conducted.

The fish oils possess a very complex composition. They contain quantities of highly unsaturated acids which are certainly dissimilar to linolic and linolenic, as is shown by the different behaviour of their brom-derivatives. The insoluble hexabromides of linolenic melt, for example, fairly sharply at 170 to 180° C., but the bromides of the fish oil unsaturated acids do not melt undecomposed, a property which enables the analyst to distinguish between the drying and fish oils.

Clupanodonic acid, $C_{18}H_{28}O_2$, which yields a typical octobromide, appears to be an essential constituent of the unsaturated portion of these oils, and this explains the difference between the melting point of the bromides of linseed and fish oils mentioned. Among the acids of the saturated group palmitic erucic and the lower volatile homologues have been detected.

The solid "stearine" consists chiefly of palmitin.

Although the palest qualities of fish oil do not possess an altogether unpleasant smell, yet the fishy odour is always in evidence, particularly in the darker oils which usually have a rank odour. The peculiar odour appears to be due to nitrogen and phosphorus compounds, and much research has been conducted with a view to deodorising the oil. The common reagents, alkali, sulphuric acid, etc., are by no means effectual, but the solid products obtained by catalytic reduction of the liquid oils are practically odourless (see Reduction of Unsaturated Acids).

CHAPTER VII

THE NATURAL WAXES, THEIR COMPOSITION AND PROPERTIES

The saponifiable Waxes consist essentially of mixtures of esters of various fatty acids with high molecular weight monovalent alcohols.

A few of the lower members of the saturated series, butyric, isovaleric, caproic, etc., have been detected in woolwax, and stearic, palmitic and oleic form a small part of the acids occurring in woolwax and sperm oil, but the more important constituents are acids of higher molecular weight.

Four acids occurring in waxes of considerable importance are:—

Carnaubic, $C_{23}H_{47}COOH$, belonging to the saturated series, occurs in carnauba and woolwaxes. It melts at 72·5° C. and is readily soluble in hot alcohol, ether and benzol, from which it crystallises in white needles.

Cerotic acid, $C_{25}H_{51}COOH$, melting at 77·8° C., is found in quantity in various waxes, notably as its ceryl ester in beeswax, from which it may be obtained by saponifying and crystallising from hot alcohol. It is practically insoluble in cold alcohol.

Two oxyacids are of interest, viz., lanopalmic, $C_{15}H_{30}(OH)COOH$ (melting point 87 to 88° C.), and lanoceric, $C_{30}H_{57}(OH)_2COOH$ (melting point 104 to 105° C.) both occur in woolwax.

The alcoholic portion of the waxes may be isolated by drying the products of hydrolysis at 100° C., and extracting with acetone. The crude alcohols may be acetylated and the acetyl derivatives separated by vacuum distillation.

The most important known representatives are given in Table on the next page.

On distillation with alkali the alcohols lose the elements of water and pass into fatty acids of similar carbon content.

WAX ALCOHOLS.

Series.	Formula.	Name.	Melting point. ° C.	Occurrence.
(*a*) Saturated.				
$C_nH_{2n+1}(OH)$.	$C_{21}H_{49}OH$	Carnaubyl	68/69	Woolwax.
	$C_{26}H_{53}OH$	Ceryl	79	Woolwax, Carnauba wax, Chinese wax.
	$C_{30}H_{61}OH$	Myricyl	68	Carnauba and Beeswax.
(*b*) Unsaturated.				
$C_nH_{2n-1}OH$.	$C_{12}H_{23}OH$	Lanolinyl	102/104	Woolwax.
(*c*) Divalent saturated.				
$C_nH_{2n}(OH)_2$.	$C_{30}H_{60}(OH)_2$	Cocceryl	101/104	Cochineal.

Cetyl alcohol forming, for example, palmitic acid,

$$C_{16}H_{33}OH \longrightarrow C_{15}H_{31}COOH + HOH.$$

The vegetable waxes are solid bodies of high melting point; in chemical properties they manifest great stability, and are much more difficult to saponify than the fats and oils, aqueous alkaline solutions being almost without action upon them. In order to completely saponify them, it is necessary to treat them at high temperatures by boiling with double normal solutions of *KOH* in 96 per cent. alcohol under pressure, or in solution of *KOH* in amyl alcohol which boils at 137° C.

It is largely to the insolubility of the high molecular weight soaps formed that the difficulty of saponification is due.

It is important to note that the yields of fatty acids from the complete saponification of waxes is only 60 to 65 per cent., as compared with 94 to 96 per cent. for the majority of fats.

Further, since the high molecular weight alcohols are insoluble in water and cold alcohol, it will be noted that there is a high percentage of so-called unsaponifiable matter obtained by the hydrolysis of waxes.

With the exception of Southern and Arctic sperm oils which

are liquid all the animal and vegetable waxes are solid at the ordinary temperatures.

We shall consider here only a few typical waxes of commercial importance, viz. :—

Carnauba wax, a solid of vegetable origin.
Sperm oil, a liquid wax of animal origin.
Spermaceti, Woolwax, Beeswax } Solid waxes of animal origin.

Carnauba Wax.—The leaves of the palm tree, *Corypha cerifera*, which flourishes in South America, yield on boiling with water a yellowish wax known as carnauba wax.

The crude dirty product is refined by remelting on boiling water and the separated wax dried and bleached by filtering through fuller's-earth. To facilitate the bleaching in this way, it is quite common to add a little paraffin wax to the crude material, whereby the melting point is lowered and more perfect decolorisation secured.

Carnauba wax contains (according to Sturcke, quoted by Lewkowitsch) "a hydrocarbon melting at 59 to 59·5° C., ceryl alcohol, myricyl alcohol, dihydroxy alcohol, carnaubic acid and an oxyacid of formula

$$C_{19}H_{38}\begin{cases} COOH \\ CH_2OH \end{cases}$$

Carnauba wax finds its chief industrial applications as a stiffener for candles and in the manufacture of waterproofing and furniture polishes.

Carnauba wax shows the following average constants:

Specific gravity at 15° C.	Melting point.	Acid value.	Saponification value.	Iodine value.	Total fatty acids, per cent.
·990	83/90° C.	2 to 4	79/80	13·5 per cent.	47·9

Beeswax, a secretion of the bee, is the principal constituent of the honeycomb.

The comb from which the honey has been extracted is melted over water and the molten wax skimmed off and passed through a filter press to remove the suspended impurities.

The crude wax so obtained varies somewhat in hardness, smell and colour according to the care with which the combs are handled and the peculiarities of the bees from which it has been procured. In general the natural wax is of a dirty yellow colour, but it can be more or less readily bleached to a fine whiteness. The wax will bleach very satisfactorily by simple exposure to light and air, but as this is too costly a procedure for general commercial purposes the bleaching is usually done by treating the molten wax with acid bichromate or other decolorising reagents.

Beeswax consists essentially of a mixture of cerotic acid and myricyl palmitate together with a few per cents. of higher alcohols in a free state. It is freely soluble in carbon tetrachloride and chloroform, but only slightly in warm alcohol.

The constants of beeswax vary widely with the source of the wax. The following table gives a few of the average figures :—

Specific gravity at 15° C.	Melting point.	Acid value.	Saponification value.	Iodine value.
·960/·970	62—68° C.	20 (about)	95 (about)	8—9%

Beeswax finds industrial application in the manufacture of candles, furniture polishes, varnishes, etc.

Woolwax is obtained in the process of wool-scouring.

The natural wax of the wool is extracted before spinning by washing with soap solutions which remove the neutral woolfat in an emulsified state. The emulsion is broken down with dilute sulphuric acid, and the mixture of fatty acids from the soap and neutral wax skimmed off, and sold as recovered grease. From this grease a neutral wax is obtained which is known in its anhydrous state as "Adeps Lanae."

The wax is capable of forming solid emulsions with water, a property upon which its use in the arts depends. The medicinal

product "lanoline" is such an emulsion containing from 20 to 30 per cent. of water.

Woolwax possesses a most complex composition, and beyond the fact that cholesterol and isocholesterol is present in quantity, little is known of its composition.

Sperm Oil and Spermaceti.—Two varieties of sperm oil are known in commerce, viz., Southern from the blubber of the Great Sperm Whale which is found in the Pacific and Indian Oceans and Arctic sperm from the Bottlenose Whale which inhabits the Arctic seas. The mode of preparation and chemical properties of these two oils are so similar that it will suffice to describe them together.

The head fat of the whale is boiled out with water, when a dirty-coloured oil is obtained. This crude oil deposits a precipitate of spermaceti on standing in the cold, and the first refinery operation is therefore to remove this product by chilling the crude to 35 to 38° F. and then pressing out the liquid, which, after bleaching with earth, is sold as winter sperm oil.

Winter sperm forms about 70 to 75 per cent. of the total weight of the crude, and is usually a clear light-coloured oil which does not deposit any precipitate at 38° F.

The crude spermaceti remaining in the filter cloths is again pressed at 50° F. to obtain a somewhat inferior quality of sperm oil known in the trade as spring sperm.

For the preparation of high grade spermaceti the residue in the bags is pressed again at 70 to 80° F., when 3 to 4 per cent. more oil exudes, and a dark brownish mass of crude spermaceti, melting from 100 to 115° F., remains.

It is of course advisable to secure the fish as fresh as possible in order to obtain a clear odourless product, but if this is not practicable, the colour and smell may be improved by refining with alkali.

Genuine sperm oil apparently contains no glycerides, but consists entirely of esters of acids of the oleic series with high molecular weight unsaturated alcohols. On treatment with nitrous acid the sperm oil acids yield a buttery elaidin.

The nature of the acids and alcohols is, however, very imperfectly known.

The more important analytical values for Southern and Arctic oils are:—

	Specific gravity, 15·5° C.	Saponification value.	Iodine value.	Free acid, per cent.	Viscosity, water at 60° F. = 1.	Alcohols, per cent.
Southern sperm	·879/·880	120/129	84/86	1·1 to 2·5	39·1	39·0
Deodorised Arctic sperm	·879/·880	123/130	80/84	1·6/2·5	41·5	39/40

From the figures it will be seen that it is quite impossible to differentiate these two varieties by chemical means, but Arctic sperm has a much more unpleasant taste and gumming tendency than Southern oil, a property probably due to the presence of more highly unsaturated acids in the former oil (Arctic elaidin is softer than Southern).

Although sperm oil possesses the lowest viscosity of any known oil, yet it is an admirable lubricant, and is largely used for the lubrication of light machinery. It is also widely employed for illuminating purposes.

Spermaceti.—Crude sperm oil yields from 10 to 12 per cent. of crude spermaceti, which is refined by boiling with dilute caustic lyes, followed by washing with hot water. The purified product is clarified and allowed to crystallise in shallow trays, and the crystals are then pressed at about 80° F.

Pure refined spermaceti forms white semi-transparent tasteless crystals, melting from 40 to 46° C. and is soluble in boiling alcohol, from which it separates on cooling in a crystalline form.

Spermaceti consists almost wholly of cetyl palmitate, and finds its chief application in the manufacture of candles.

CONSTANTS OF SPERMACETI.

Specific gravity at 15° C.	Melting point.	Saponification value.	Iodine value.	Alcohols, per cent.
·910/·960	41/46° C.	121/129	3·8	51·5 to 54·2

CHAPTER VIII

ANALYTICAL METHODS

THE analysis of an oil or fat is carried out with the object of deciding either its

(1.) Purity (*i.e.*, freedom from adulteration, etc.).

(2.) Suitability for some particular purpose, such as soap-making, burning, etc.

(3.) Composition (*i.e.*, content and nature of glycerides, unsaponifiable matter, etc.).

The last-mentioned type of investigation is rarely necessary in technical practice, and is generally a matter of more or less scientific interest. The technical analysis therefore aims solely at the estimation of certain factors, from a study of which the purity and suitability for any particular purpose can be gauged.

We shall consider the analytical methods under the following headings:—

(1.) Quantitative estimation of the non-fatty constituents.

(2.) Qualitative tests.

(3.) Determination of the physical constants.

(4.) Quantitative reactions.

The first operation in the analysis of any oil or fat is the removal and estimation of mechanical impurities, such as water, sand and non-fatty organic matter, (tissue, leaves, fibre, etc.). The pure specimen thus obtained is then subjected to certain qualitative tests, and finally examined by a series of quantitative reactions. By the former one can detect the presence of substances such as rosin oil, mineral oil, soaps and paraffin, and by the latter means the percentage of any of these present, or, if the sample is a pure fatty mixture, the relative proportions of its constituent oils within limits may be determined.

Estimation of Water.—The presence of appreciable quantities,

i.e., 0·2 per cent. and over, of water in an oil or molten fat, is visible to the eye as a turbid emulsion, but for the detection of minute quantities in cases where absolute dryness is essential (insulating oils) a few cub. centimetres are shaken in a test tube with white anhydrous copper sulphate. In the presence of 0·001 per cent. of water the copper salt turns greyish green. An alternative method, which the present author has found very successful for the detection of minute traces of water in hydrocarbon oils, is to immerse a pellet of metallic sodium in the oil and note the evolution of bubbles of hydrogen gas. For the estimation of the water content 5 to 10 grammes of the fat are weighed into a small shallow dish provided with a stirrer and heated on a sand bath at about 110° C., preferably with the addition of a few cub. centimetres of absolute alcohol. The hot mixture is continuously stirred until frothing ceases. The dish, rod and fat is then weighed again; the loss in weight is water. This method, however, cannot be used if the oil contains easily volatile substances or soaps. In this case a known weight of the substance is shaken with 100 cub. centimetres of anhydrous petroleum ether, and allowed to stand in a graduated cylinder. The water settles out, and may be read off. Occasionally, however, emulsions form, which separate badly in this process, and when this is found to occur, it is better to treat the fat with xylol and distil (Marcusson).

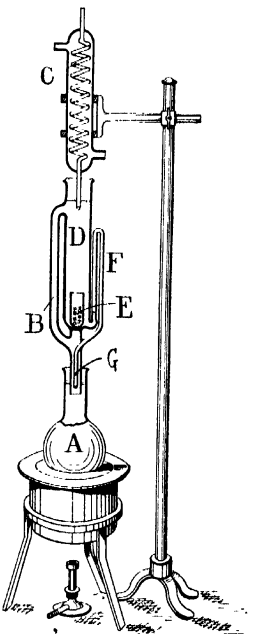
20 to 100 grammes fat are mixed with 100 cub. centimetres of xylol, and introduced into a litre flask. The flask is then connected to a condenser and heated in an oil bath. The distillate, which consists of water and xylol, is collected in a graduated cylinder. When all the xylol has distilled over, the volume of the water which settles out in the cylinder is read off.

Mechanical Impurities.—Grit, tissue, etc., is estimated by dissolving a known weight of the oil in light petrol ether, and filtering the solution through a weighed filter paper. The residue on the filter is washed with petrol until the filtrate is free from fat. The filter paper is then dried in the water oven and weighed. The increase in weight represents the mechanical impurities.

Determination of Fat Content.—When large quantities of non-fatty matter are present, and generally in the estimation of the

amount of oil in various materials, it is usual to extract the fat by means of a solvent. This is usually carried out by means of Soxhlet's extraction apparatus, an illustration of which is given below.

The substance to be extracted is wrapped in a piece of filter paper, or porous thimble (*E*), and placed in the extractor (*D*). A tared flask is then attached (*A*) and the whole connected to a reflux condenser (*C*) and heated by a water bath. The solvent is vaporised, and rises through the side tube (*B*); is condensed in the reflux and drips back on to the substance contained in the extractor, where it continues to collect until the top of the side tube (*F*) is reached. When this occurs the whole of the liquid is syphoned off through (*F*) and returned to the flask by the tube (*G*). The solvents usually employed are ether, chloroform or carbon tetrachloride, and the process is allowed to run for at least four hours, after which the whole of the solvent is returned to the flask, which is then removed, the solvent distilled off, and the residual fat dried at 110° C. and weighed.



SOXHLET'S EXTRACTION APPARATUS.

FIG. 4.

Determination of Ash.—Many oils contain appreciable quantities of inorganic matter, either combined as soap, or accidentally acquired impurities. To determine the amount of these, 10 grammes of the sample are weighed into a tared platinum dish and very carefully heated until the oil takes fire. When all the volatile matter has been removed, the dish is heated with the blow-pipe until all the carbon is consumed. The residue left is the ash.

Mineral Acids and Alkali.—Mineral acids in oil are detected by

shaking 100 cub. centimetres of hot oil with 50 cub. centimetres of water in a separating funnel. The funnel is then placed in the steam oven until all the water has separated. The water is then drawn off, allowed to cool, and tested with a few drops of methyl orange solution. In the presence of mineral acids, a deep red tint is produced.

Alkalis, free and combined, may be similarly detected by phenol-phthalein. Since, however, soaps in watery solution colour phenol-phthalein, free alkali cannot be detected by this means, but only by dissolving the oil in a mixture of neutral alcohol and ether, and applying the phenol-phthalein test. The production of a pink colour in this test demonstrates the presence of free alkali.

Sulphur and Nitrogen.—These elements are detected by strongly heating five or six drops of the oil with a small pellet of metallic sodium in a hard glass test tube. The tube is then broken by dipping while red hot into a beaker of water. After filtering, the aqueous solution is divided into two portions. To one a few drops of a dilute solution of sodium-nitro-prusside is added. The minutest trace of sulphur colours the solution violet red. The other portion is boiled with a crystal of ferrous sulphate, and acidified with *HCl*. A blue precipitate or coloration indicates the presence of nitrogen.

Special Qualitative Tests.

Detection of Rosin Oils in Fatty Oil.—One or two cub. centimetres of the oil are shaken in the cold with an equal volume of acetic anhydride, and allowed to stand until separation is complete. The under-layer of acetic anhydride is then drawn off by a fine pipette and poured through a filter paper previously moistened with acetic anhydride into a clear dry tube. One drop of sulphuric acid (sp. gr. 1·53) is added. If rosin oil be present a violet coloration is produced (Liebermann-Storch).

Detection of Heavy Mineral Oils.—Mineral oil is practically insoluble in 96 per cent. alcohol, but all fats dissolve fairly readily. Accordingly, if 10 cub. centimetres of oil be shaken with 90 cub. centimetres of 96 per cent. alcohol at room temperature, and then allowed to stand, the bulk of the mineral oil present

will settle out (Holde). This method applies equally well to the detection of paraffin wax in fatty oil.

Besides these tests, which are extremely useful to indicate the nature of the substance under examination, there are a great many reactions which depend upon the production of certain colours, when the oil is treated with various reagents. Formerly these colour tests were considered as the most important means of detecting adulteration and admixture which the analyst could apply, but nowadays they are chiefly used as confirmatory tests to the quantitative reactions. Three of the most important colour tests are (*a*) the Halphen test for cotton seed oil, (*b*) the Badouin reaction for Sesamé oil, and (*c*) the Welman reaction for vegetable oils.

(*a*) **Halphen's Test.**—Two cub. centimetres of the oil are mixed in a test tube with a few drops of amyl alcohol, and an equal volume of a 1 per cent. solution of sulphur in CS_2. The tube is heated for twenty to thirty minutes in the boiling water bath, CS_2 being added from time to time to make up for the evaporation. If the oil contains not less than 5 per cent. of cottonseed oil, a distinct red colour is developed. By heating the mixture in a closed soda-water bottle at 100° C. the reaction may be made more sensitive, and even 1 per cent. of cotton oil may be detected in admixture with other oils and fats. Like all colour tests, however, this reaction is not an infallible guide, since cotton oil which has been previously heated to 250° C. or treated by chlorine or sulphurous acid, no longer shows the colour. Further, the fat of animals fed on cottonseed cake frequently contains the chromogenous substance of cotton oil, and consequently some lard oils show this reaction. The colour is probably produced by the presence of a small quantity of an unsaturated acid in the oil with which the sulphur combines to form a chromophoric sulpho-ketone.

(*b*) **Badouin's Reaction for Sesamé Oil.**—A solution of 0·1 gramme of sugar in 10 cub. centimetres of *HCl* (sp. gr. 1·19) is prepared. To this solution 20 cub. centimetres of the oil is added, vigorously shaken, and then allowed to stand until the acid layer separates. In the presence of 1 per cent. of sesamé oil a red colour is produced. The reaction depends upon the

formation of furfurol from the sugar, which then combines with the constituents of the sesamé oil to form a colour stuff. Hence the test may be carried out by using furfurol instead of sugar and *HCl*, in which case the reaction is slightly more sensitive. A somewhat similar reddish coloration is produced by olive oils from certain sources, and also occasionally in the fat of animals fed on sesamé cake.

(*c*) **Welman's Reaction for Vegetable Oils.**— This reaction depends on the property possessed by oils of vegetable origin to reduce phosphomolybdic acid. One gramme of the fat or oil is dissolved in chloroform and treated with 2 cub. centimetres of a freshly prepared solution of phosphomolybdic acid, and a few drops of nitric acid. Vegetable oils produce a greenish colour, which turns blue on addition of alkali. This reaction is of very doubtful value, since it has been shown that many rancid fats which contain aldehydes are capable of bringing about reduction. For the accurate detection of vegetable oils the phytosterine test is the only reliable guide.

Detection of Cholesterine and Phytosterine in Fats and Oils.

As mentioned above, by far the most satisfactory means of distinguishing between oils of vegetable and animal origin is the isolation and examination of the unsaponifiable matter. It has been pointed out before that all natural fats contain a small quantity of non-glyceridic constituents, and in the case of the animal oils this substance always contains appreciable quantities of cholesterol, while those of vegetable origin contain phytosterol. Accordingly, the detection of one or other of these compounds in an oil or fat may always be taken as indicating the source from which it has been obtained. Cholesterol and phytosterol are distinguished from one another by the difference in their crystalline form and the melting point of the free alcohols and their acetates. Most animal fats contain from 0·1 per cent. to 0·5 per cent. of cholesterol, but all vegetable oils contain at least 0·2 per cent. to 1·2 per cent. of phytosterol. Cholesterol melts at 148·4°—150·8° C., and is apparently a chemical individual. But phytosterol melts varyingly from 135 to 144° C., according to the source from which it is obtained and the method of isolation.

It is probably a mixture of isomorphous bodies. The acetate test is far more sensitive than the examination of the crystals, but the latter method is much quicker and quite reliable when large quantities of plant oils are present. For the isolation of the unsaponifiable matter for investigation, it is best to work upon 100 grammes of fat, although 10 per cent. of vegetable in animal oil can be detected in 50 grammes. The method is as follows:

One hundred grammes or aliquot part of fat is placed in a litre flask and saponified with 200 cub. centimetres of 20 per cent, alcoholic potash until a clear soap solution is obtained. This solution is then brought into a 2-litre separating funnel, and the flask washed out with 500 cub. centimetres of warm water, which is added to the alcoholic solution in the funnel. Eight hundred cub. centimetres of ether are now added, the funnel stoppered, and shaken under the tap for one minute. After allowing to separate, the soap solution is drawn off and the ether evaporated in a 1½-litre flask. The soap solution is again washed twice with 300 cub. centimetres of ether each time, which ether is then added to the residue from the distillation and all the ether driven off.

To ensure complete removal of all soap and unsaponified fat, the residue from the ether is again boiled with 10 cub. centimetres of the 20 per cent. alcoholic potash for ten minutes, transferred to a funnel, diluted with 30 cub. centimetres of water, and extracted three times with 100 cub. centimetres of ether each time. On distilling off the separated ethereal solution, a waxy or crystalline residue, remains, which consists of the crude cholesterol or phytosterol. The raw product is boiled with 20 cub. centimetres of absolute alcohol, filtered hot, and allowed to crystallise spontaneously in a flat dish. After standing for one to two hours, crystals begin to appear. If the solution contains almost wholly cholesterol, these crystals begin to form at the surface as thin plates; but if phytosterol predominates, crystallisation begins at the walls of the vessel and extends outwards in needle-like shapes. At this stage a few drops of the liquid are placed on a microscope slide and viewed under a low power in strong daylight, preferably assisted by polarised light.

If cholesterol alone is present, thin rhombic plates are seen, as illustrated in the diagram (Fig. 5), and the presence of animal oil in the sample examined is proved. If little or no cholesterol be present (*i.e.*, if the solution contains only phytosterol), the crystals present a very different appearance. They consist of thin needles which, when allowed to form slowly from dilute solutions, may be as much as 1 centimetre long, and from concentrated solutions appear as fine, short rods (Fig. 6). When, however, a mixture of both cholesterol and phytosterol in about

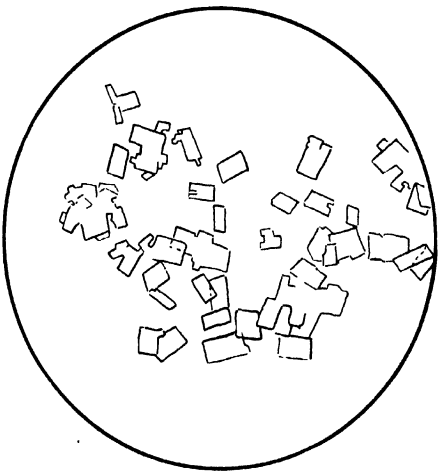


FIG. 5.—Microscopic appearance of Crystals of Cholesterol.

equal quantities is present, the cholesterol crystal does not form, but phytosterol is seen. With a large preponderance of cholesterine, mixed crystals, whose shape is dissimilar to either, occur. Consequently it will be seen that the test is much more sensitive for vegetable than for animal oils in admixture.

The main bulk of the crystalline solution is now taken and evaporated to dryness on the water bath. Two or three cub. centimetres of acetic anhydride are then added, brought to the boil for one minute, and then the excess of acetic anhydride gently evaporated off. The crystals of acetate are dissolved in a little hot alcohol and allowed to stand at ordinary temperatures until

crystallisation is complete. The crystals are then filtered off, again dissolved in alcohol, and re-crystallised. It is advisable to repeat the process three times, after which the crystals are washed free from mother liquor, dried, and introduced into a capillary tube attached to a thermometer bulb, and the melting point determined.

Phytosterol acetate melts at 125·6°—137° C.

Cholesterol acetate melts at 114·3°—114·8° C.

Mixtures of the two show intermediate melting points of

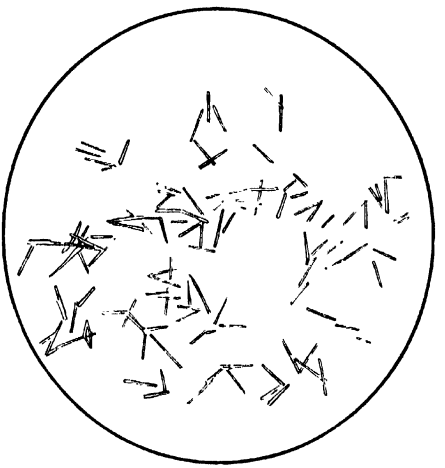


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FIG. 6.—Microscopic appearance of Crystals of Phytosterol.

unreliable value. We can say, however, that if the melting point is above 115° C. phytosterol is present.

Bomer has shown that by means of this test even the 1 per cent. of vegetable oil may be detected in admixture with animal oil. If, however, the sample contains wool fats or paraffin, the phytosterol test is no longer applicable, since the former contain other higher alcohols and the latter lowers the melting point below that of cholesterine. Accordingly the conclusions to be drawn must always be modified by a consideration of the other analytical constants.

The detection of animal oils in admixture with vegetable oils

is much more difficult, because, as will be seen from the foregoing, a very small amount of phytosterol suffices to spoil the appearance of the characteristic cholesterine crystal. For this purpose it is best to determine the melting point of the free alcohol. Cholesterol melts at 148·4°—150·8° C., while phytosterol fuses between 135° and 143·8° C. Hence, although a melting point above 144° C. may be taken as definite evidence of the presence of cholesterol, it does not follow that a lower temperature of fusion indicates its absence.

The more important physical constants are:—

A. The specific gravity.
B. The melting and solidifying points.
C. The viscosity.
D. The refractive index.

Occasionally a knowledge of the flash-point, specific heat, heat of combustion, dielectric strength and capillarity is of value. The physical properties of the individual oils are fairly constant, and serve to some extent to characterise them. The physical methods possess the advantage of being simply and quickly performed.

Specific Gravity.—The specific gravity is the ratio of the weight of a given volume of the oil to that of an equal volume of water. Strictly speaking, the determination should always refer to the same temperature for both water and oil. For convenience, this temperature is generally 15·5° C. (60° F.) for liquid oils, and 100° C. (212° F.) for solid fats. Since, however, a given weight of water has a minimum volume at 4° C. (maximum density) some analysts prefer to express the ratio of the oil at 15·5° C. to that of water at 4° C., which consequently gives the "density" of the sample at the temperature specified. In order to avoid confusion over this nomenclature, it is always advisable to indicate the standard of comparison. Thus when the gravity is referred to water at the same temperature it is usual to write $\frac{15{\cdot}5^\circ\,C.}{15{\cdot}5^\circ\,C.}$ or $\frac{100^\circ\,C.}{100^\circ\,C.}$ as the case may be; but if the sample is compared with the water at 4° C., one writes $\frac{15{\cdot}5^\circ\,C.}{4^\circ\,C.}$ or $\frac{100^\circ\,C.}{4^\circ\,C.}$

The systems $\frac{15{\cdot}5^\circ\text{ C.}}{4^\circ\text{ C.}}$, $\frac{100^\circ\text{ C.}}{4^\circ\text{ C.}}$ give results 0·09 and 4·3 per cent. lower than that of $\frac{15{\cdot}5^\circ\text{ C.}}{15{\cdot}5^\circ\text{ C.}}$, $\frac{100^\circ\text{ C.}}{100^\circ\text{ C.}}$ respectively. The coefficient of expansion of oils varies from ·000675 to ·000727. Hence it is unnecessary to adjust the temperature of the oil to exactly 15·5° C., since it may be assumed for practical purposes that the gravity changes ·0007 for 1° C.

The specific gravity of fairly limpid oils is conveniently and quickly determined by means of the hydrometer. The hydrometer employed may be graduated either to read off direct specific gravities, or may indicate values on some arbitrarily fixed scale. Of the latter type are the Beaumé and Twaddle hydrometer. The relation between these scales is here shown:—

$$\text{Sp. gr.} = \frac{144{\cdot}3}{134{\cdot}3 + n\text{Bé}}\text{ (light Beaumé).}\quad \text{Sp. gr.} = \frac{\frac{n(Tw)}{2} + 100}{100}$$

The specific gravity balance gives more accurate values than the hydrometer for limpid oils, but cannot be used for oils of high viscosity. For the determination of the specific gravity of very viscous oils and molten fats, the specific gravity bottle or pyknometer must be used. The sample is warmed until fairly limpid, and then poured into the bottle. When all air bubbles have been removed, the bottle and its contents are brought to the required temperature by immersion in a vessel of water and allowed to stand. The perforated stopper is then introduced, allowing the excess oil displaced by the stopper to ooze through the hole, the bottle dried and weighed.

Melting Point.—Since the fats and oils are not chemical individuals, but mixtures of varying composition, they do not melt sharply at a definite temperature, but gradually soften as the temperature rises until the whole mass becomes fluid. Further, the melting point of a fat is affected by the method of preparing the sample, it being observed that the temperature of fusion of a specimen which has only just solidified is different from the melting point of the same sample after standing in the cold for some hours, owing to the fact that in the former case crystallisation has not reached completion. Hence for determination of

the melting point care must be taken to allow the sample to stand for some hours before making the test.

The simplest method consists in dipping a glass tube of about 1 millimetre bore open at both ends into the molten specimen, and, after setting aside in a cold place overnight, fastening the tube to the bulb of a thermometer immersed in a beaker of water.

The water is carefully heated up with constant stirring until the fat slides up the tube and floats as a liquid drop on the surface of the water.

This method is, however, obviously unsuitable for lubricating greases, which frequently contain soap, etc., soluble in water. In this case the procedure is as follows: A narrow test tube is fitted round the bulb and lower part of the stem of a thermometer, the bulb of which has been smeared with the grease, and the tube immersed in a bath of water or oil. Heat is then applied to the beaker until the grease melts and runs down the bulb forming a clear drop on the bottom.

The **viscosity** of a liquid is defined as the resistance of its particles to change their shape or shear, and may be measured by observing the time taken for a given quantity of the liquid to flow through a narrow capillary tube. The relations are expressed by "Poiseuilles'" equation:—

$$y = \frac{\pi r^4 pt}{8vl}$$

Where y = coefficient of absolute viscosity

r = radius of tube

l = length of tube

v = volume of liquid passing through in the time t, and

p = pressure on unit cross-sectional area of the liquid in the tube.

In practice it is quite unnecessary to express the results in terms of absolute viscosity, since only comparative values are required.

A simple type of viscometer suitable for comparative work may be made with an ordinary pipette enclosed in a water-jacket.

The oil to be tested is sucked up into the pipette and prevented from flowing out until the desired temperature has been attained by placing hot or cold water, as the case may be, in the jacket.

The oil is then allowed to flow out, and the time taken for a given volume to escape is noted. Much more satisfactory results are

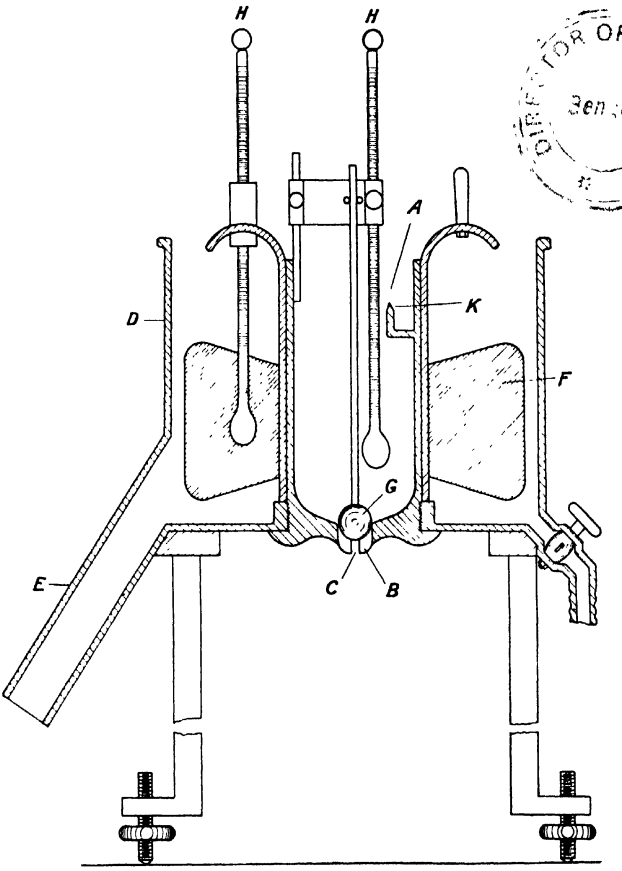

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FIG. 7. Boverton Redwood's Viscometer.

obtained, however, by using a standard instrument such as Engler's or Redwood's. The construction of Redwood's viscometer will be seen from the figure.

A is a silvered copper cylinder about $1\frac{7}{8}$ by $3\frac{1}{2}$ inches.

B is an agate plug fitted to the bottom of the cylinder through which a small hole *C* has been drilled.

The cylinder is surrounded by a copper water bath *D* provided with a leg *E* for heating the water and rotating vanes *F* to assist in maintaining constant and even distribution of the temperature. The hole in the agate is closed by a plunger *G*, and thermometers *IIII* are placed in the oil and water.

The cylinder is filled with the oil to be examined up to the top of the little pointer *K*, and when the desired temperature is reached the plunger is lifted off the hole and the oil collected in a graduated flask. The time taken in seconds for 50 cub. centimetres to flow out gives the viscosity of the sample in arbitrary units.

The average viscosity of rape oil at 60° F. is 535 seconds; hence

Relative viscosity at *x*° F. (rape oil at 60° F. being taken as 100)

$$= \frac{Td \times 100}{535 \times \cdot 9142}.^{1}$$

T = time taken for outflow of 50 c.c. of oil of density d.

Refractive Index.—The simplest type of refractometer is Abbes', an illustration of which is shown. It consists of two prisms of highly refracting glass, between the faces of which a drop of the fat or oil to be examined is squeezed.

The two prisms when lying on one another form a solid rectangular block, A, B, C, with a layer of oil in the centre. The prisms are capable of rotation about a horizontal axis, the angle turned through being indicated by the pointer on the scale. A beam of light, reflected by the mirror R and transmitted through the prisms, is viewed by the telescope F, and the prisms slowly rotated until total reflection of the light occurs at the oil layer. The critical angle is then read off on the scale, which is usually graduated to give direct readings of refractive index.

The determination of refractive index affords a simple, quick, and most valuable guide in the detection and identification of adulteration of oils and fats.

[1] ·9142 = density of Rape oil.

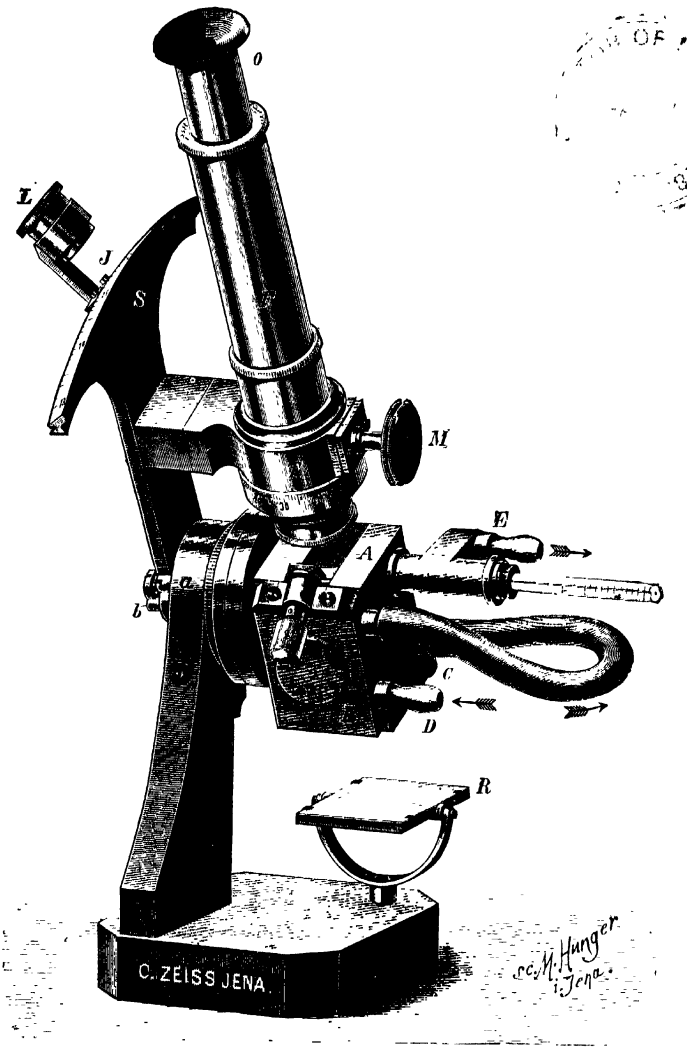


FIG. 8.—Refractometer.
(By permission of Messrs. Carl Zeiss (London) Ltd.)

Quantitative Reactions.—The qualitative tests applied to oils, as mentioned above, can only be considered as affording confirmatory evidence of the nature or purity of the sample.

In order to indicate with certainty the composition and properties, it becomes necessary to subject the fat to certain processes which can be quantitatively measured. These are known as the quantitative reactions.

The examination of a large number of representative samples of any fat or oil known to be genuine reveals the fact that a few of these quantitative reactions always show within certain limits the same value for that particular class of fat, *e.g.*, 1 gramme of olive oil always requires about 185—190 milligrammes of *KOH* to completely saponify it, while a similar weight of rape oil requires 170—179 milligrammes of *KOH* (saponification value). The saponification value is therefore called a "constant" of the oil.

The chemical constants are:—

1. The saponification value.
2. The iodine value.
3. The acetyl number.
4. The Reichert-Meissl value for volatile fatty acids.
5. The Hehner value (content of insoluble fatty acids).
6. The hexabromide number.

Of these the first two are the most important in general analytical work.

Besides these constants there are quantitative reactions which vary appreciably in different samples of the same oil, according to its age, method of preparation, etc. These are the "Variables." The more important variables are:—

1. The acid number.
2. The glycerine value.

The Saponification Value *is the number of milligrammes of caustic potash required to completely saponify* 1 *gramme of the fat* (Kottesdörfer), *or the number of grammes of caustic potash required to saponify* 100 *grammes of fat* (*percentage saponification value*).

It has been pointed out on p. 85, that when an alkali acts ide a salt of the fatty acid (soap) is produced, and l liberated. If the reaction be conducted in watery

solution hydrolysis of the soap occurs, giving rise to an alkaline reaction, and hence an accurate determination of the neutral point is impossible. Accordingly, in order to determine the saponification value, a solvent which cannot hydrolyse the soap formed must be employed. For this reason, and also on account of the greater rapidity of hydrolysis, the reaction is always carried out in alcoholic solution. The method of procedure is as follows:—

One to two grammes of the fat are weighed out into a clean, dry flask, 25 cub. centimetres $\frac{N}{2}$ alcoholic potash solution being added. The flask is then fitted to a reflux condenser and gently boiled for 30 to 40 minutes. The condenser is then removed and the contents of the flask titrated with $\frac{N}{2}$ *HCl*, using phenol-phthalein as indicator. A blank test is carried out under similar conditions.

The difference in the number of cub. centimetres between the blank and the oil test gives the amount of alkali which has combined to form neutral soap, and this number, multiplied by 28[1] and divided by the weight of the sample taken, gives the saponification value.

Example: 1·5 grammes fat were saponified with 25 cub. centimetres $\frac{N}{2}$ alcoholic *KOH* solution. On titration 15 cub. centimetres of $\frac{N}{2}$ *HCl* were required. The blank test required 24·8 $\frac{N}{2}$ *HCl*. Hence the difference, 24·8—15=9·8.

$$\text{Saponification value } \frac{9{\cdot}8 \times 28}{1{\cdot}5} = 182{\cdot}9.$$

Care must be taken to avoid access of CO_2 into the potash; otherwise the sensitiveness of the end point is destroyed, since CO_2 reacts acid towards phenol-phthalein. Where the sample is very dark in colour, as in the case of compounded cylinder oils, it is difficult to see the colour change of the indicator. Various means of overcoming this difficulty have been described, but it is the

[1] One cub. centimetre $\frac{N}{2}$ *HCl* is equivalent to ·028 gramme *KOH*, *i.e.*, 28 milligrammes *KOH*.

author's experience that by diluting the solution after saponification with a relatively large volume of neutral hot alcohol and titrating over a white surface, using ten drops of phenol-phthalein to 100 cub. centimetres liquid, the end point is readily detected.

The presence of mineral or resin oils in admixture with animal or vegetable is readily detected by the lowering of the saponification value, from a knowledge of which the percentage of each of the former bodies present can be calculated.

Example: A sample of rape oil adulterated with mineral oil gave a saponification value of 150 (saponification value of genuine rape averages 175).

Hence, since

175 milligrammes *KOH* are required by 1 gramme pure rape

$\therefore$ 150 „ „ would saponify only 0·85 gramme „

$\therefore$ 1 gramme of the sample contains 0·85 gramme rape

i.e., the sample contains 15 per cent. mineral oil.

The Iodine Value *is the number of grammes of iodine absorbed by* 100 *grammes of oil*, and is a measure of the degree of unsaturation of the glycerides contained in the oil. There are two ways of carrying out the test, viz., by Hubl's process and the Wij modification. As the latter method possesses many advantages, and is most usually employed, we shall describe it in detail.

Wij's solution is prepared by dissolving separately in glacial acetic acid 9·4 grammes ICl_3 and 7·2 grammes iodine. The solutions are then mixed and made up to 1 litre. This gives a solution of iodine monochloride in glacial acetic acid. The same result is attained if we dissolve 13 grammes of iodine in a litre of acetic acid and pass in chlorine until the change in colour indicates that all the iodine has been converted into iodine monochloride. At this point the titre is exactly doubled. A $\frac{N}{10}$ solution of sodium thiosulphate is prepared by dissolving 25 grammes of the pure salt in 1 litre of water. In order to standardise the thiosulphate, a solution of 3·8666 grammes of pure potassium bichromate in 1 litre is used. 20 cub. centimetres of this bichromate solution, when mixed with 10 cub. centimetres of 10 per cent. potassium iodide and 5 cub. centi-

metres of concentrated *HCl* liberates 0·2 gramme of iodine, which is then titrated with thiosulphate, using starch paste as indicator, until the blue coloration just disappears.

The estimation of the iodine value of the oil is carried out as follows:—

0·5—1 gramme of solid fat, or 0·15—0·25 gramme of liquid oil, is weighed out into a perfectly dry, clean, stoppered bottle of about 300 cub. centimetre capacity, and dissolved in pure carbon tetrachloride. 25 cub. centimetres of the standard iodine monochloride solution is added, the bottle quickly stoppered and well shaken, and allowed to stand in a cool, dark place. With non-drying oils, half an hour suffices to complete the absorption; semi-drying oils require forty to fifty and drying oils sixty to seventy minutes. When the absorption is complete, 20 cub. centimetres of 10 per cent. potassium iodide solution is introduced into the bottle and 150 cub. centimetres of distilled water, care being taken to wash the iodine solution off the stopper into the bottle. The mixture is then titrated, after the addition of 2 cub. centimetres starch paste, until the blue colour just disappears on shaking.

A blank test is performed under similar conditions, and the difference in titre between the two tests, indicates the weight of iodine absorbed by the given weight of oil.

Example: 0·2 gramme of rape oil was taken and 25 cub. centimetres iodine solution used. After standing for fifty minutes the excess iodine required 20 cub. centimetres of the standard thiosulphate.

The blank required 30·5 cub. centimetres thiosulphate.

Difference 30·5 − 20 = 10·5 cub. centimetres thiosulphate.

Hence, iodine absorbed equals 10·5 × ·0197.[1]

∴ Iodine value or (*i.e.*, iodine absorbed 100 grammes fat) = $\frac{10{\cdot}5 \times {\cdot}0197 \times 100}{0{\cdot}2} = 103{\cdot}4$.

Hubl uses instead of ICl a solution of iodine and $HgCl_2$ in alcohol. The method of procedure is similar to that described above, but the length of time required for absorption (twelve to eighteen hours) militates against its use.

[1] 1 cc. Thio was equivalent to 0·0197 gramme iodine.

The advantages of Wij's solution over Hubl's is:—

1. The time required for absorption is much shorter.
2. The solution keeps its titre for a considerable time.

Wij found that a solution which required 56·46 centimetres thiosulphate immediately after preparation had only changed to 56·27 one week later. The method gives almost theoretical values for semi-drying oils and acids, but in working with highly unsaturated bodies it is very important to maintain the conditions absolutely the same in comparing a series of samples. Particularly, the length of time allowed for absorption must be the same in all cases.

Wij's method gives higher values than Hubl's for mineral oils and cholesterol.

The iodine value is one of the most important analytical constants of fats and oils. It is customary to speak of those oils, which absorb over 120 per cent. of iodine as "drying oils," while those having an iodine value between 95 and 120 are called "semi-drying," and those below 95 "non-drying oils." The iodine value of the highly unsaturated oils falls somewhat after long storage, even when contained in closed barrels, owing to the slight oxidation and polymerisation taking place.

Hexabromide Value.—The bromides of oleic and linolic acids are soluble in ether, but the compounds obtaining by brominating linolenic and other highly unsaturated acids are insoluble in ether. Hence the determination of the percentage of bromides insoluble in ether yielded by an oil is a valuable means of estimating its contents of glycerides containing three or more double bonds.

One to two grammes of oil are dissolved in a mixture of 40 cub. centimetres pure ether and 5 cub. centimetres glacial acetic acid. The flask is carefully protected from absorbing moisture, immersed in ice water, and bromine added drop by drop until the red colour persists. Allow to stand in the ice water for four to five hours, and then filter. Wash the precipitate four times with 10 cub. centimetres each time of cold ether, and dry the residue of insoluble bromides at 100° C. till constant. Nondrying and semi-drying oils yield practically no insoluble bromides, but linseed and fish oils give a large percentage.

The Acetyl Value.—When a compound containing an hydroxyl group is boiled with acetic anhydride, the *H* atom of the *OH* group becomes replaced by the acetyl radicle CH_3CO, *e.g.*,

$$2C_nH_{2n+1}(OH).COOR + \begin{matrix} CH_3.CO \\ \diagdown \\ O \\ \diagup \\ CH_3.CO \end{matrix} \longrightarrow 2C_nH_{2n+1}(OCOCH_3).COOR$$

The acetylated compound may be saponified with potash

$$C_nH_{2n+1}(OCOCH_3).COOR \longrightarrow C_nH_{2n+1}(OH).COOR + CH_3.COOR$$
$$\downarrow H_2SO_4$$
$$CH_3COOH + K_2SO$$

and the amount of acetic acid liberated determined.

The Acetyl Value.—*The number of milligrammes of caustic potash required for the neutralisation of the acetic acid obtained on saponifying one gramme of an acetylated oil, fat, or wax, is known as the acetyl value,* and is a measure of the number of hydroxyl groups contained in the oil.

The determination of the acetyl value was first described by Benedikt, and has been modified by Lewkowitsch, who gives the following description of the process: "10 grammes of the oil are boiled with twice the amount of acetic anhydride for two hours in a round bottom flask, attached to an inverted condenser.

"The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 or 600 cub. centimetres of boiling water, and heated for half an hour, whilst the slow current of carbon dioxide is passed into liquid through a finely drawn out tube reaching nearly to the bottom of the beaker to prevent bumping. The mixture is then allowed to separate into two layers, the water syphoned off, and the oily layer again boiled out, in the same manner three successive times. The last trace of acetic is thus removed, which is ascertained by testing with litmus paper.

"Prolonged washing beyond the required limit causes slight dissociation of the acetyl product, which would lead to too low an acetyl value. The acetylated product is next filtered through a dry filter paper, in an oven, to remove water. About 3 grammes of the acetylated product are then saponified by boiling with alcoholic potash, as in the determination of the saponification value. The alcohol is evaporated off, and the soap dissolved in water. From this stage onwards, the determination

is carried out either by (*a*) the distillation process, or (*b*) the filtration process." In the distillation process the solution of soap and potassium acetate, is acidulated with dilute sulphuric acid, and distilled in a current of steam, until 600 to 700 cub. centimetres of water are distilled off. The distillate containing the acetic acid is titrated with decinormal potash, using phenolphthalein as an indicator. The number of cub. centimetres used multiplied by 5·61 and divided by the weight of substance taken, gives the acetyl value.

In the filtration process a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic caustic potash employed is added to the soap solution. The mixture is warmed gently, until the fatty acids collect on the surface as an oily layer. These fatty acids are filtered off and washed with boiling water until the washings are no longer acid, and the filtrate may be titrated with decinormal alkali. The acetyl value is then calculated in the same way as described above.

Pure glycerides containing no hydroxyl groups show no acetyl value.

Castor oil, however, shows a definite acetyl value, owing to the presence of the hydroxyl group in its constituent, ricinolein

$$C_3H_5[OC_{18}H_{32}O(OH)]_3$$

The determination of the acetyl value gives a ready answer if it be required to decide the quantity of an hydroxylated oil (*e.g.*, castor) in the presence of other non-hydroxylated oils, because the pure triglycerides containing no *OH* group give no acetyl value.

If, however, the sample contains some mono or diglycerides, the free *OH* of the glycerol will acetylate, and too high a value be obtained.

$$C_3H_5\begin{cases}OH\\OR\\OR\end{cases} \longrightarrow C_3H_5\begin{cases}OCOCH_3\\OR\\OR,\ \text{etc.}\end{cases}$$

The number of cub. centimetres of decinormal potash required to neutralise the soluble volatile fatty acids from 5 *grammes of a fat, is known as the Reichert-Meissl value.* This value is quite

arbitrary, and so the estimation must always be carried out in exactly the same way. The method employed is as follows: 5 grammes of the pure melted fat is introduced into a 200 cub. centimetre flask, and saponified by 2 grammes of solid potash dissolved in 50 cub. centimetres of 70 per cent. alcohol. The flask is heated on the water bath with frequent shaking to evaporate off the alcohol completely, when the resultant soap paste is dissolved in 100 cub. centimetres of water and acidified with

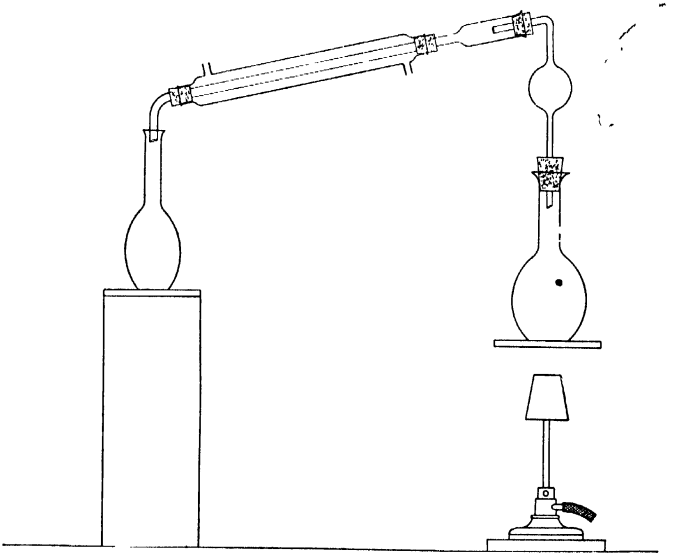


FIG. 9.—Distillation Apparatus for Determination of Volatile Fatty Acids.

40 cub. centimetres of 10 per cent. sulphuric acid. A few pieces of pumice are then thrown into the flask, which is fitted to a T piece, provided with a bulb, and connected to a Liebig's condenser.

The watery solution of soluble and volatile acids is distilled carefully so that about 2 cub. centimetres per minute of distillate passes over, until 110 cub. centimetres have been collected. The distillate is then filtered into a 100 cub. centimetre graduated flask and the solution of volatile fatty acids titrated by decinormal

potash, using phenol-phthalein as indicator. The number of cub. centimetres used multiplied by 1·1,[1] is known as the Reichert-Meissl value.

A blank test should be carried out side by side with the sample investigated in order to obviate any error which might arise from the presence of traces of aldehyde or acid in the alcohol.

For the majority of fats and oils, the Reichert-Meissl value is below 1·0, but a few, such as coconut oil, butter fat, palm-nut oil, and other less known oils, contain considerable quantities of volatile fatty acids, and hence possess relatively high Reichert-Meissl value. Determination of this constant, therefore, is of considerable value in indicating the presence of oils of this type in mixtures. The quantity of volatile fatty acids present in an oil varies somewhat with the age and purity of the sample; old specimens generally show higher values than fresh oils.

The Hehner Value *is the percentage of insoluble fatty acids and unsaponifiable matter in the oil.* 5 grammes of fat are saponified in an open dish by boiling with 40 cub. centimetres $\frac{N}{2}$ *KOH* and 10 cub. centimetres water. When all the oil has disappeared the alcohol is evaporated off, the soap dissolved in 200 cub. centimetres of hot water, and then acidified by dilute H_2SO_4. The hot liquid is allowed to stand until the fatty acids form a clear layer at the top; the mixture is then filtered through a wet filter-paper and the fatty acids remaining on the paper continuously washed with hot water until the filtrate is no longer acid to litmus.

The insoluble fatty acids remaining behind are then washed off the filter paper by hot alcohol into a tared dish, and after evaporating and drying at 110° C. for one hour they are weighed. The dish may be again dried at 110° C. for half an hour, and weighed again till two consecutive weighings give practically the same result. Absolute accuracy is not possible, since the acids gain a little by oxidation, and lose a little by volatilisation.

With the exception of butter fat, coconut and palm-kernel, the Hehner value of the commoner oils and fats lies between 94 and 96·1.

[1] 100 cub. centimetres only taken from a total of 110 cub. centimetres.

The **Acid Number** *is a measure of the amount of free fatty acids present in the oil or fat, and is defined as the number of milligrammes of KOH required to neutralise the free acids in* 1 *gramme of the fat.*

Since the free acids in the majority of fats and oils are palmitic, oleic and stearic, it is quite satisfactory to assume a mean molecular weight of 282 for the acids, and hence to express the acidity in terms of free oleic acid per cent. For many purposes the latter mode of expression is the better.

5—10 grammes of the oil is dissolved in hot neutralised alcohol and titrated with $\frac{N}{10}$ *KOH* alcoholic potash solution, using phenolphthalein as indicator. From the number of cub. centimetres of $\frac{N}{10}$ alkali used, the acid value can be calculated.

1 cub. centimetre $\frac{N}{10}$ *KOH* is equivalent to ·0056 gramme *KOH*

or 0·0282 gramme oleic acid.

Note.—If the percentage of free acids is small, *i.e.*, if only a few cub. centimetres of alkali are required, aqueous *KOH* may be used, but if a large quantity of potash is necessary it is essential to use alcoholic *KOH*, otherwise the excessive dilution of the alcohol with water will hydrolyse the soap and interfere with the sharpness of the end point.

The Glycerine Value.—The most satisfactory method of estimating glycerol is to convert it into its acetyl derivative by boiling with acetic anhydride, and then determine the acetic acid yielded by saponifying the triacetin.

$$C_3H_5\begin{cases}OCOCH_3\\OCOCH_3\\OCOCH_3\end{cases}$$

20—25 grammes of oil are accurately weighed off, saponified with alcoholic *KOH*, and the alcohol then evaporated off on the water bath. The soap paste is dissolved in water, and the fatty acids liberated by sulphuric acid and filtered off. The filtrate containing the glycerol is neutralised with barium carbonate and evaporated to partial dryness. The residue is then extracted with

alcohol-ether, and the solution containing the glycerol, mixed with traces of impurities, is gently heated in the water bath to remove the alcohol and ether, dried in vacuo and weighed.

In an aliquot part the glycerol is then determined as follows:

About 2 grammes of the crude glycerine, obtained as described above, is heated with 7 to 8 cub. centimetres of acetic anhydride and 3—4 grammes of anhydrous sodium acetate, for about one and a-half hours in a round-bottomed flask provided with a reflux condenser.

The triacetin so produced is carefully dissolved in 100 cub. centimetres warm water and filtered. The excess of acetic acid in the filtrate is neutralised very carefully with *NaOH*. The neutral solution of triacetin is then boiled with 25 cub. centimetres of double normal alkali for half an hour, when the excess of alkali is titrated back with normal acid.

One cub. centimetre $\frac{N}{1}$ acid is equivalent to 0·03067 gramme glycerol. The percentage of pure glycerol in the crude glycerine and the amount of crude obtained from the given weight of oil being then known, a simple calculation gives the percentage of glycerol contained in the oil or fat.

No fixed scheme for the identification of an oil or separation of the individual components in a mixture can be given. The analyst must learn to take advantage of any peculiarity that may present itself, and compare the sample with oils of known purity and origin. Certain broad lines of examination, however, may be suggested. First, the odour of the specimen will be noticed, and the presence of fish, tar, or resin oils indicated, assuming that the sample does not contain some perfume, added with the object of masking the odour of its constituents. The saponification value will then be determined, and if this is found to be very low, the presence of mineral or resin oils will be suspected, and separately examined for by the qualitative test for these particular substances. The iodine value will enable us to decide, taken in conjunction with the saponification value, whether highly unsaturated oils are present, which suspicion may be confirmed or negatived as the case may be, by determina-

tion of the percentage weight of hexabromides obtained from the oils.

The colour tests for sesamé, cottonseed, etc., are also of great assistance, but, as already pointed out, complete reliance cannot be placed on them, a study of the quantitative reactions being the only true guide. Among the physical constants the refractive index is of pre-eminent importance, but the specific gravity and melting point serve in general only as confirmatory evidence where mixtures are concerned.

It is a good plan to carefully compare the results obtained from each test, as it is made with the figures for samples of known composition when further tests and lines of enquiry will invariably be indicated.

It frequently happens that the analyst has to examine mixtures of fats and oils with non-fatty matter, such as lubricating greases, soaps, etc.

In such cases the first operation is to separate as far as possible the fatty from the non-fatty, and examine each separately. This may be done, of course, in the case of a grease or soap by macerating the sample with ether or ligroin, and then shaking with dilute *HCl* in a separating funnel, whereby the fatty acids liberated from the soap, together with the oily matter, are dissolved in the ether layer, while the water—soluble and insoluble non-fatty matters are found in the lower layer, either in solution or suspension.

The fatty matter is then obtained by evaporating off the ether, and examined by the general methods outlined above, the aqueous solution or suspension forming a problem in general analysis, a consideration of which is outside the scope of this volume.

CHAPTER IX

INDUSTRIAL APPLICATION OF FATS AND OILS

Burning Oils—Edible Oils and Margarines—Polymerised, Boiled and Blown Oils—Turkey Red Oils.

A LARGE quantity of oils and fats are utilised in the arts directly and without any chemical treatment beyond that of refining. Into this class fall burning oils, edible oils and lubricants.

The bulk of the fatty oils produced, however, form the raw materials of other industries, such as soap and candle-making, boiled and blown oils, textile oils, etc.

These industries fall naturally into two main classes, namely:

(1) Industries in which the oil or fat is subjected to chemical or physical treatment, without saponifying it;

(2) Industries based upon the saponification of the oil.

Among the direct industrial uses of the oils, one of the oldest is the preparation of burning oils. A large number of the vegetable and fish oils are used directly as illuminants (such as olive, rape, whale and sperm oils), but the solid fats like tallow, require to be converted into candles before being employed for illuminating purposes. The method of employing the liquid oils as illuminants is well known, and depends upon the ability of the oil to ascend by capillary action, a wick immersed in it.

The oil on the wick is ignited, and at the high temperature converted into a number of decomposition products, which form an inflammable gas. The illuminating power of the various vegetable fats and oils differ only slightly, but in general it may be noted that the drying oils tend to thicken and clog the wick, and consequently do not find much application for this purpose. An oil intended for use as an illuminant must be carefully freed from all traces of mineral acids, salts, and alkalies, and should not contain more than 5 to 6 per cent. of free fatty acids, since all these impurities exert an injurious effect upon the wick.

Accordingly, the process of refining a burning oil consists in the main of a refinement by sulphuric acid or caustic, followed by a perfect washing with water, and then allowing to stand until completely clarified.

Pure saponifiable oils are largely used for illuminating purposes, but it is very common nowadays to add mineral illuminating oils in certain proportions to the fatty oil.

The utilisation of the oils as lubricants has been described in the chapter on Mineral Oils.

Edible Oils, Fats and Butters.

In general all vegetable and animal oils and fats which contain no substances obnoxious to the smell or taste may be used for the food of man.

In this country the demand for solid fats or butters is considerably greater than for liquid oils as a food-stuff, but on the continent of Europe and elsewhere enormous quantities of edible liquid oil is consumed.

We may consider on the one hand the production of edible oils, and on the other hand the preparation of solid fats and butter substitutes (margarines).

The more important liquid oils which are used for edible purposes are olive, sesamé, arachis, cottonseed, rape and linseed.

The best oils are obtained from fresh seeds by cold pressing, and the refining operations aim at removal of free fatty acids, colour stuffs and objectionable volatile matter. The purified oil must then be allowed to stand till all mucilage and water, which would have a tendency to induce rancidity, has settled out.

Acids must never be used in the purification of oils intended for food, since, however carefully the oil is subsequently washed, traces of decomposition products formed by the action of the acid remain in the oil and impart to it a highly unpleasant taste.

Alkali, alkaline earths and carbonates may, however, be used to extract the free fatty acids, and the volatile matter is generally removed by boiling the oil with water or blowing steam through it.

The neutralised oil is finally filtered through charcoal or earth

to bleach and remove the last traces of water, after which it is allowed to clarify.

Oils intended for table use should always remain clear even in the cold, and in order to satisfy this condition most oils require "demargarinating." Demargarination consists in allowing the oil to cool until it deposits the stearines of relatively high melting point dissolved in the oil.

This process is usually carried out by chilling the oil artificially, and then either drawing off the supernatant layer of clear liquid or better by centrifuging the mass. The success of this operation depends upon the production of definite crystals or granules of stearine, which can only be obtained by comparatively slow cooling to slightly below the depositing temperature. If the oil is rapidly chilled to a low temperature the crystals have not time to grow into large aggregates, but are precipitated through the oil in a fine state, forming a broth which will not settle, and is very difficult to separate either by filtration or centrifuging.

For example, when olive oil is kept for some time at 5° C., large masses of stearine settle out and the clear oil can easily be decanted, whereas if the oil is quickly cooled to 0° C., fine particles of stearine remain suspended throughout the oil.

An edible oil must always be free from rancidity, but need not be neutral—in fact a little free acidity imparts a piquant flavour to the oil, and it is almost entirely by its taste that the oil is valued.

It is quite common practice to blend several oils together in order to obtain the desired flavour.

A large branch of the edible fat industry is nowadays concerned with the manufacture of

(1) Lard and suet substitutes for cooking purposes.

(2) Butter substitutes (margarine).

When premier jus, obtained in the rendering of beef fat, is cooled and pressed, it is separated into two portions—about 40 per cent. of a solid stearine of high melting point called beef stearine and a liquid or buttery mass known as oleo oil or oleo margarine passes through the press cloths.

The former material is used in the preparation of suet and lard substitutes, while the oleo oil goes to the margarine maker.

The **suet substitutes** are made by melting together at the lowest possible temperature mixtures of beef stearine and liquid vegetable oils, such as cotton, sesamé, etc., and churning up the mixture while it spontaneously cools. By this means the stearine crystals are broken up and intimately mixed with the liquid portion, the whole forming a homogeneous mass of a greater or lesser degree of hardness, according to the relative proportions of oil and stearine and the temperature.

The **lard substitutes** are somewhat softer than the suet substitutes, and usually contain some genuine lard.

A frequent mixture is made of choice steam lard, tallow stearine, mutton tallow and cottonseed or sesamé oil, the relative proportions being varied at different seasons of the year. The oils and fats are melted together in tin vessels at a low temperature, and then rapidly chilled by pouring on to cylinders through which ice water is circulating to bring about solidification of the stearine throughout the mass (lard coolers).

Margarine.—When an oil or molten fat is violently churned up with water in the presence of albuminous or protein matter, an emulsion is produced consisting either of minute watery drops suspended in oil or of globules of oil surrounded by water or aqueous solution. Milk is a typical example of the latter type of emulsion, and butter is constituted on the former basis, *i.e.*, it is an emulsion of water, or rather watery solutions, in a semi-solid fat.

The art of margarine making therefore consists in mixing oils and fats until a blend of suitable firmness or softness is obtained, and then vigorously agitating the molten fats with a certain percentage of skimmed milk (watery fluid).

The emulsion which forms is then rapidly chilled, which causes the fats to solidify, thus thickening the mass and so rendering the emulsion stable.

The process is carried out as follows:—A mixture of oleo margarine, beef stearine, cottonseed, sesamé or other vegetable oil is prepared in such proportions as may be required to produce a blend of suitable melting point. The mixed fats are then melted in tinned vessels at as low a temperature as possible. Meanwhile a certain quantity of skimmed milk (which has been

previously pasteurised) is run into a jacketed pan, provided with an agitator and a movable lid.

The milk is warmed to about 20° C., and violently agitated while the molten fatty mixture is slowly run in. When the emulsification is judged to be complete the mixture is rapidly cooled, withdrawn from the stirring pan, and placed on cold slabs for a few hours. The margarine so produced is an emulsion of water in fat, but always contains in addition large drops of water embedded in the mass. To remove these and to improve the texture of the product, the crude buttery mass (with salt added) is placed on rotating tables across which steel rollers revolve. By this means the excess of water is squeezed out and the emulsion perfectly blended into a homogeneous block, which is then cut to the required size and packed. In order to simulate genuine butter more closely "butter essences" and colour stuffs are frequently added. The essences are made from volatile acids and esters, while the colours may be methyl orange or any of the harmless yellow synthetic dyes.

Needless to say, highly refined and purified fats and oils must be used, and the art of the manufacturer lies in compounding or blending the fats and oils, and in producing perfect emulsification by careful attention to the details of temperature, time of stirring and preliminary treatment of the milk. Too high a proportion of stearines tends to import a tallowy taste, while too much oil gives an unctuous feel and flavour to the margarine. Further, there can be no doubt that the degree of dispersion of the watery liquid throughout the mass, *i.e.*, the fineness or coarseness of the globule, exercises marked influence upon the flavour, and this factor is dependent not only on the mode of stirring, but also on the nature of the fats employed, their glycerides and free acids.

Vegetable Butters.—The great demand made on animal fat during recent years has resulted in the utilisation of the vegetable fats, coconut and palm-kernel oils in the manufacture of margarines. Such mixtures are made in exactly similar plan to that described above, the solid vegetable fats taking the place of the animal stearines.

Much discussion has arisen as to the relative digestibility of the margarines and genuine butters, and the matter has not

received very definite evidence either way from experiment. It would not be surprising, however, in view of experiments in other directions to find genuine butter more digestible owing to its content of minute amounts of enzymes, ferments, etc., which may influence digestive processes.

Margarine has been the subject of legislation in every country, and its sale under the description "butter" has been universally prohibited.

The German law requires the addition of sesamé oil to all margarines in order to facilitate its detection in German butters suspected of adulteration.

The analysis of a typical sample of margarine is compared with genuine butter in the table below:—

	Fresh English Butter.	Margarine.
Fat . . .	83·87	82·02
Casein . .	2·72	0·74
Salts . . .	0·42	5·23
Water . .	12·99	12·01
	100·00	100·00

Boiled Oils, Polymerised Oils, Blown Oils.

On exposure to air and light for varying periods all oils undergo a change differing in degree according to the quantity of unsaturated glycerides present. As a result of such oxidation and possibly polymerisation, the specific gravity and viscosity rises, while the iodine value falls, and in the case of the highly unsaturated oils even solidification may occur.

For example, a sample of olive oil (according to Holde and Winterfeld), after standing exposed to light and air in a flask for twenty-one months, showed a rise in specific gravity from ·914 to ·916 at 15° C., an increase in viscosity from 563 to 588 seconds (Engler), and a decrease of 4 per cent. in iodine absorption.

A specimen of rape oil on exposure to air in a shallow dish for

six months increased in viscosity from 704 to 1200 seconds, with a concomitant rise in gravity, and linseed oil, as is well known, "dries," after a few days exposure in thin films, to a hard mass.

Somewhat similar changes in gravity and viscosity may be produced in certain oils by heat alone in the absence of air, and as the reaction in this case evidently differs from the foregoing in that it cannot be due simply to oxidation, it is convenient to distinguish between the two processes.

This distinction is marked also by differences in chemical composition, oils of the former class containing a much smaller quantity of ether insoluble oxyacids than those which have been subjected to the action of heat and air.

As types, it will suffice to consider the products obtained by heating tung and linseed oils in the absence of air.

When tung oil is heated for a short time at about 200° C. it passes into a solid gelatinous mass, and, since the phenomenon occurs when air is excluded, some explanation other than oxidation must be looked for. Tung oil consists essentially of the glyceride of elæo-margaric acid, an unsaturated liquid containing two double bonds. On standing exposed to light this acid slowly passes into a solid isomeride, to which the name elæostearic has been given.

It is possible that the gelatinisation of tung oil is due to this isomerisation just as oleic passes into elaidin, but on the other hand Lewkowitsch has pointed out that the fatty acids of gelatinised tung oil possess a much greater molecular weight than those of the original oil, from which it would appear that the solidification is due, at any rate partially, to the condensation or uniting together of two or more molecules of the glyceride, a reaction which is known as polymerisation. The solidified mass on this view would be **polymerised tung oil.**

A somewhat similar change takes place when linseed oil is heated to 300° C., air being excluded. The oil thickens, becomes specifically heavier and shows a diminution in the iodine value.

As the yield of insoluble bromides from the heated oil is considerably less than from the original, it would indicate that we have here again to do with a polymerisation of the unsaturated linolene, which view is supported by the observed increase in molecular weight of the oil. On the other hand, the rise in the

acetyl value which such treatment always produces points to a more deep-seated change than that of simple polymerisation, and suggests that intermolecular change of some kind accompanies the polymerisation.

Our knowledge of these processes, however, is but slight and stands in urgent need of investigation, both from the standpoint of organic and physical chemistry.

The polymerised linseed oils are used as binding material in the manufacture of printers' ink, etc.

When linseed oil is heated to moderately high temperatures in the presence of air a somewhat different change takes place, and a so-called boiled oil results. These boiled oils when exposed to the air in films dry more quickly than the raw oil, and so the process is employed for the preparation of oils for painting, varnishing, etc.

For the preparation of best boiled linseed for painters' use, good Baltic oil, freed from moisture and mucilage by long standing, is heated to about 150° C. in iron vessels by means of steam coils for four to six hours with small quantities of oxides of lead or manganese, a current of air being blown through the mass for a short time.

During the process the products of decomposition which form bubble through the oil and escape, giving the surface the appearance of ebullition, from which the term "oil boiling" is derived.

Although a little acrolein is evolved, it is found that the bulk of the glycerol is unaffected by the process, and, further, the decomposition does not proceed far enough to give rise to hydrocarbons in any quantity, nor is the iodine absorption affected to a great extent. Some idea of the changes which occur may be gathered from the table below, wherein the original raw oil is compared with the boiled oil obtained from it by heating for four hours at 160° C. with ·5 per cent. of lead-mangano drier.

—	Sp. Gr. at 15° C.	Saponification Value.	Iodine Value.	Insoluble Bromides.	Unsaponifiable Matter.	Reichert-Meissl.
			Per Cent.	Per Cent.	Per Cent.	
Raw oil .	·932	190·1	188·0	28·0	0·20	0·0
Boiled oil	·943	185·5	179·2	16·5	0·37	0·11

The chemical reactions which occur when an oil "dries" are by no means completely understood, nor is the composition of the "dried" product known with any degree of certainty. It has, however, been shown by Bauer and Hazura that the oxidation results not only in the saturation of the unsaturated linkages with oxygen, but hydroxyl groups are formed.

Further, the more linolenic glycerides present the quicker is the drying, but linolenic acid, linseed oil fatty acids, or their ethyl esters do not dry in the same way as the glycerides. Since the drying is undoubtedly accelerated by previously heating the oil to a temperature which brings about a certain amount of polymerisation, it would appear that the drying process is a combination of polymerisation and oxidation phenomena.

The time taken for a linseed oil to dry is much reduced when the oil contains a minute percentage of salts of lead or manganese, colophony, turpentine, etc., the latter substances being looked upon as "catalysts." The physico-chemical mechanism of this catalytic action has recently been studied by Fahrion and Genthe.

It was noticed by Schonbein in 1858 that when a substance is slowly oxidised spontaneously in the air, one portion of the oxygen combines with the compound undergoing oxidation, while another part of the oxygen is rendered "active," and may at the same time oxidise some other substance.

For example, ozone appears to be always formed during the oxidation of phosphorus by air.

Engler has suggested the name "autoxidiser" for the substance undergoing oxidation (in this case phosphorus), and "acceptor" for the body which unites at the same time with the activated oxygen. Fahrion applies this idea to the drying of linseed oil.

The driers (autoxidisers) spontaneously take up oxygen, being converted into peroxides, while the oil simultaneously "accepts" the active oxygen.

On the other hand, he considers it possible that it is a case of autocatalysis, in which the drier acts as a "pseudo-catalyst" by assisting the formation of an oxygen derivative (peroxide) of the glycerides which can itself accelerate the drying process.

Fahrion leaves the decision of these two alternatives open, but Genthe, as the result of his experiments on the reaction velocity,

votes for the latter hypothesis, a view which would receive support from the well-known fact that drying can take place in the total absence of a "drier," in which case a minute amount of the "peroxide" of the oil must be considered as already formed and capable of reproducing itself.

Blown or Oxidised Oils.

It has been pointed out already that all oils can absorb oxygen to greater or lesser degree, becoming thereby thicker and specifically heavier, and the velocity and extent of the reaction may be considerably increased by blowing air through the hot oils.

The oils usually employed for this purpose are the semi-drying and whale oils, partly because the non-drying are too inert and the drying oils too reactive, absorbing oxygen to form products which tend to gum and gelatinise, and so are unfit for many of the purposes for which the "blown" oils, obtained from semi-drying material, are used.

The blowing process is carried out by heating the oil to 60°—80° C. in cylindrical tanks provided with a steam jacket and perforated coils through which air is forced, while the mass is kept in a state of vigorous agitation in order to permit the oil to come into contact with as much air as possible. As a result of the reaction which takes place, sufficient heat is evolved after a few minutes to enable the action to proceed without the aid of steam, and, indeed, it is frequently necessary to moderate the action by passing cold water through the jacket.

As with the polymerised and boiled oils, the exact nature of the change is unknown. Hydroxyl groups are unquestionably formed, as the considerable rise in acetyl value proves.

Influence of air blowing Rape Oil for fifteen hours at 40 to 60° C.

—	Sp. Gr. at 60° F.	Viscosity in Seconds (Redwood) at 100° F.	Iodine Value.	Acetyl Value Per Cent.
Original oil . .	·9150	114	99·2	0·82
After blowing . .	·9592	660	65·5	7·29

The thickened oils are miscible with mineral oils, and are used in admixture with the latter for lubricating.

Sulphonated Oils (Turkey-red Oils).

Turkey red or alizarine oil is prepared by acting upon castor oil at about 40° C. with concentrated sulphuric acid.

The sulphonated oil so formed is washed with water in which sulphate of soda is dissolved (to avoid troublesome emulsions), and the purified compound neutralised by sodium carbonate or ammonia.

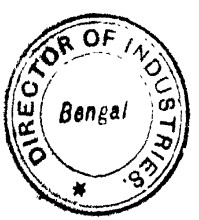
The product, which is either completely soluble in cold water or readily emulsiable, is employed in dyeing.

The reactions which take place are complicated, and the sulphonated oil contains a mixture of several substances.

Richardson and Walton have isolated from a Turkey-red oil compounds of the following composition :—

$$C_{17}H_{32}(So_4Na)CO.ONa$$
$$\diagup OH$$
$$C_3H_5—OH$$
$$\diagdown OCOC_{17}H_{32}SO_4Na$$

and the lactone of ricinoleic acid.



DIRECTOR OF INDUSTRIES
Bengal

CHAPTER X

SAPONIFICATION OF FATS AND OILS ON A TECHNICAL SCALE

The Distillation of Fatty Acids—Oleines and Stearines.

$$C_3H_5\begin{cases}OR+HO.H\\OR+HO.H\\OR+HO.H\end{cases}\rightarrow C_3H_5\begin{cases}OH\\OH\\OH\end{cases}+3\,ROH$$

The above equation shows that under the action of water a glyceride may be split up into its constituent acids and glycerol, the process being one of water absorption to which the term hydrolysis has been given.

Now this hydrolysis can be brought about at all temperatures by mixing pure water with the oil, but the time taken to decompose the glyceride is, among other things, proportional to the temperature.

For example, when cottonseed oil is subjected to the action of steam at 220° C. about 21 per cent. is hydrolysed in two hours, but at 165° C. about seven hours is required, and on simple boiling with pure water at 100° C. over 100 hours is required to bring about this amount of hydrolysis.

Further, since the reaction is reversible, *i.e.*, free acids and glycerol tend to recombine, forming glyceride, complete hydrolysis is not possible, even by prolonged action at very high temperatures, unless some of the free acids formed are continuously removed or fixed. This is usually accomplished by mixing an alkali or alkaline earth with the oil undergoing change.

If a strong base, such as caustic soda or potash, is used, complete saponification is possible by simply boiling the oil and alkaline solution together for a few hours.

It is important to bear in mind that this latter process really

consists of two separate and independent reactions which progress side by side according to the equations

$$(a)\quad C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+\begin{matrix}HOH\\HOH\\HOH\end{matrix}\quad C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+3\,ROH$$

$$(b)\quad 3\,ROH+3\,NaOH\quad 3\,RoNa+3\,HOH.$$

The velocity of hydrolysis by water can be enormously increased by adding to the water so-called catalytic agents, such as acids, ferments and enzymes. For example, Lewkowitsch has shown that when cottonseed oil is boiled with HCl (sp. gr. 1·16) for twenty-four hours, over 85 per cent. of the oil becomes hydrolysed.

This accelerating action is due really to the high concentration of the hydrogen ion in acid solutions, for it has been shown that the velocity of hydrolysis is proportioned to the concentration of the hydrogen ion.

It was mentioned in the paragraph on castor oil that the castor seed contains appreciable quantities of a fat-splitting enzyme, and several patents have been taken out for the use of this enzyme as a catalyst in large-scale hydrolytic operations.

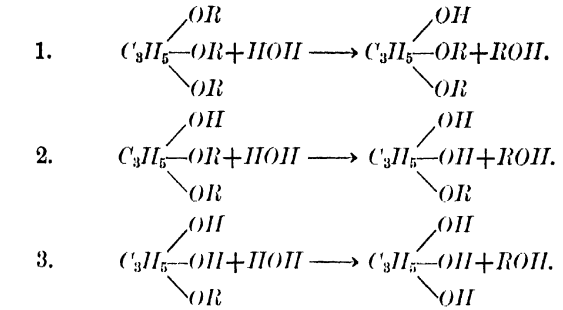
Whatever method of hydrolysis be employed, it is obviously very important to facilitate the reaction by mixing the oils with the aqueous solutions as intimately as possible, *i.e.*, a good emulsion must be produced.

The formation of emulsions is greatly assisted by using a sulpho-aromatic compound, prepared by dissolving oleic acid in an aromatic hydrocarbon and acting on the solution with sulphuric acid. This reagent, named after its inventor Twitchell, is largely used in the saponification of fats and oils.

Theory of Hydrolysis.

It was originally thought that the hydrolysis of a glyceride was a simple and direct reaction in which the three acyl groups were split off together. Alder Wright, and later Geitel, have, however, investigated the process, and concluded that the reaction proceeds in successive steps, di- and mono-glyceride being first formed as intermediate compounds, which subsequently break into glycerol and acids.

These successive steps are illustrated in the following equations :—



This view has been supported by Lewkowitsch, who, among other things, detected the presence of dierucin in an old sample of rape oil. The intermediate bodies have, however, not yet been isolated from fat partially saponified by steam or alkali.

It is possible to decide questions such as these by determining the velocity constants of the reactions, and efforts are now being made to accurately measure these values. The evidence up to the present remains rather incomplete, but it has been shown that the reaction is by no means simple, and is modified somewhat according to the method of saponification employed.

Enormous quantities of oils and fats are hydrolysed by boiling solutions of caustic alkalis for the manufacture of soap, but for those industries which require a supply of pure fatty acids (candle-making, etc.), saponification must be conducted by other means. Superheated steam alone will bring about a high degree of saponification, and indeed systems have been employed using this reagent alone, but the high temperature necessary tends to produce an excessive darkening in colour of the acids, and further, owing to the reversibility of the reaction, a few per cents. of fat always remain unacted upon. Hence this process has given way to the following methods of saponification :

(1) The autoclave process.
(2) The acid process.
(3) The Twitchell process.
(4) The enzyme process.

(1) **The Autoclave Process.**—This process was introduced by Milly in 1851, and is nowadays employed in the glycerine and, to some extent, candle and soap industries.

The molten fat is run into a cylindrical iron vessel and mixed with from 1 to 3 per cent. of lime or magnesia. The autoclave is then closed and steam at 6 to 8 atmospheres allowed to act on the mixture, which is kept in agitation for six to eight hours. When hydrolysis is complete the steam is shut off and the mixture of acids, soap and glycerine water drawn off into a tank, well washed with hot water to remove the glycerine, and the supernatant fatty acids and soaps are finally boiled with the requisite amount of dilute H_2SO_4 to decompose the soaps.

The following table (due to Lewkowitsch[1]) shows the velocity of the hydrolysis of tallow mixed with 3 per cent. of lime under 10 atmospheres pressure.

1 hour	. .	38·6 per cent. free acids.
2 hours	. .	77·4 „ „
3 „	. .	83·9 „ „
4 „	. .	87·5 „ „
5 „	. .	88·6 „ „
6 „	. .	89·3 „ „
7 „	. .	93·0 „ „
8 „	. .	97·5 „ „
9 „	. .	98·1 „ „
10 „	. .	98·6 „ „

From this it will be seen that the fat is rapidly saponified at first until about 75 per cent. has been converted, after which the reaction gradually slows down and rarely exceeds 99 per cent. at the end of twelve hours.

The quantity of undecomposed fat still left in the mixture is dependent upon the temperature, percentage and nature of base, and also on the composition of the fat itself, coconut oil, for example, being much more resistant to decomposition than tallow.

This process gives a satisfactory yield of glycerine, but the fatty acids are somewhat darker than the fats from which they are made. For the soap-maker this is a drawback, but for the manufacture of candle stearines it is of less consequence, since the acids are usually subsequently distilled.

[1] Lewkowitsch, Chem. Tech. Oils, Fats and Waxes, vol. iii.

(2) **The Acid Process.**—In technology, concentrated sulphuric acid is employed to saponify the fat because this acid acts much quicker than hydrochloric.

The fat is first heated to 120° C. to get rid of water. The molten fat is then run into a cylindrical mixing machine and violently churned up for 20 to 30 minutes with 4 to 6 per cent. of sulphuric acid of 66° Be. The action is very energetic, heat is developed, sulphurous acid evolved, and the mixture becomes black. It is important to use acid of the correct strength, because dilute acids possess relatively little hydrolytic power viewed from a technical standpoint. When the action is judged to be complete, which is ascertained by testing a sample, the black mixture is boiled up with water, when the acids rise to the surface and the glycerine water containing sulphuric acid run off.

The composition of the acid mixture before treatment with water has not been fully studied, but it undoubtedly must consist chiefly of mixtures of sulphonated fatty acids, sulphuric esters of glycerol, free sulphuric acid and various products of secondary reactions, and, as the process of hydrolysis is essentially one of "water" absorption, the mixture at this stage can scarcely be called a saponified mass. What we have, however, is a mixture of compounds which are readily split up on boiling with water into true saponification products. This is supported by the observation of Geitel that the action of H_2SO_4 on olive oil results in the formation of an additive compound of glyceride and sulphuric acid of formula

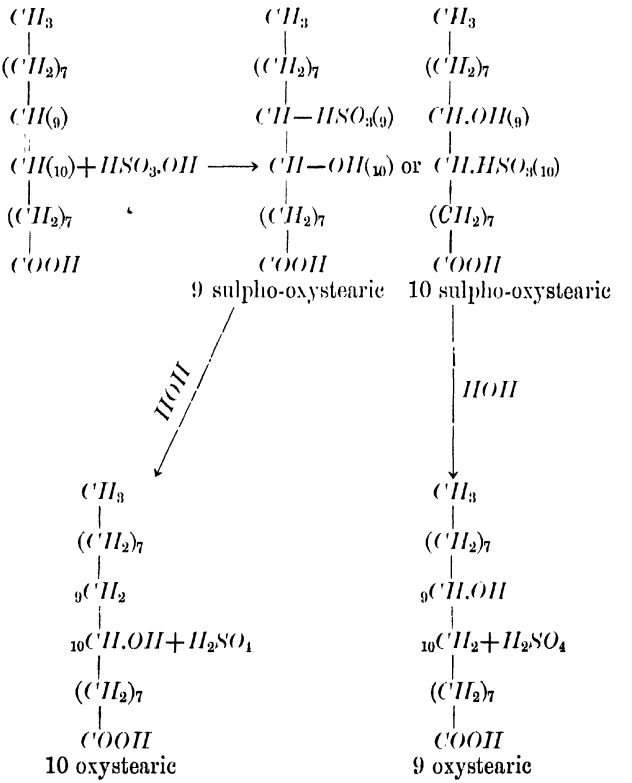
$$C_3H_5\begin{cases}OC_{18}H_{33}O \\ -OC_{18}H_{34}SO_4H.O \\ OC_{18}H_{34}OHO\end{cases}$$

and also of the well known action of sulphuric acid on glycerol, forming glyceryl sulphates which are immediately hydrolysed by water. The fatty acids themselves are no doubt sulphonated to some extent, the unsaturated in particular being transformed into sulphonated acids by addition of H_2SO_4 at the double bond.

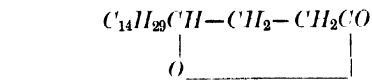
Consequently one must regard the process of boiling with water after the action of the acid as not simply one of washing out the sulphuric, but rather as the true saponification process.

The fatty acids obtained by this means are very dark in colour, and must always be purified by distillation before they can be used for candle or soap-making.

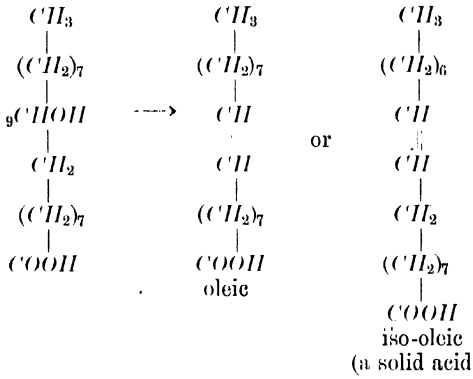
The yield of glycerol from the acid saponification is less than from the autoclave process, quantities of glycerol being destroyed by the acid; hence the best quality of fats are usually treated by the latter method in order to secure the maximum yield of the valuable glycerine. On the other hand, a higher percentage of solid fatty acids is obtained by the acid than by the autoclave process. This is due to the conversion of a portion of the oleic acid into the solid isoleic acid according to the following scheme (Lewkowitsch):



10 oxystearic on distilling loses water passing into a 7 lactone



which goes over unchanged, while 9 oxystearic loses water internally, passing into oleic or isoleic, according as the right or left *H* atom is removed, thus:—



(3) The Twitchell Process.

As already mentioned, the velocity of hydrolysis is greatly increased by forming an intimate mixture of oil and water, as one would expect, since the surface exposed to the action of the reagent is thereby increased.

Twitchell observed that when about 3 per cent. of a sulpho-aromatic compound was added to a mixture of water and fat containing traces of free fatty acids, a powerful emulsion could be produced which, when heated for a short time in a current of steam, readily saponified. The first operation in this process consists in boiling the fatty matter with a dilute solution of sulphuric acid to remove all foreign impurities; the fat is then placed in large wooden vessels provided with perforated steam coils, mixed with half its weight of water, and 2 per cent. of the reagent. The whole mass is next agitated by open steam, by means of the perforated coils. When saponification is complete,

which happens at the end of about one hour, dilute sulphuric acid is added to break down the emulsion, and the mixture allowed to stand in the warm until the fatty acids rise in a clear layer to the top, leaving the glycerine water below. The yield from this process is about the same as from the autoclave method, but the product is somewhat darker in colour and needs to be treated by distillation. It is possible to obtain practically complete saponification, and for the treatment of low-class fats the process is admirably suitable. The exact composition of Twitchell's reagent and its method of preparation is protected by patents, but similar compounds may be prepared by dissolving oleic acid in benzol, naphthaline or anthracene, and acting upon the solution with concentrated sulphuric acid.

It appears to act partly by giving up its sulphuric acid in a nascent state and partly by its emulsifying effect.

Twitchell's process differs from the acid saponification, in that it yields no solid acid from oleic since the presence of water dilutes the sulphuric to such an extent that no addition compound is possible.

(4) The Enzyme Process.

The hydrolysis of a fat by water is greatly assisted by the presence of a small quantity of certain hydrolytic or fat-splitting enzymes which act as catalysts. Hydrolytic enzymes are found in many seeds and certain organs of the animal body. They appear to be constituted like the proteins but comparatively little is known at present either of their composition or mode of action. Since the enzymes, unlike the true ferments, are not living matter they are frequently spoken of as "unorganised ferments."

Only two enzymes have hitherto been employed to bring about hydrolysis of oils and fats on a technical scale viz., those from the castor seed and the pancreas of the ox.

The purified fat or oil is mixed with 2 to 5 per cent. of a paste made by macerating castor seed meal with water. The mass is violently churned up with water containing traces of manganese salts, which accelerate the process, until a strong emulsion is formed. This emulsion is placed in wooden vats and maintained

at about 30° C. for two to three days when a high degree of saponification is reached. Although an excellent method from the theoretical standpoint, the enzyme process, owing to the slow-

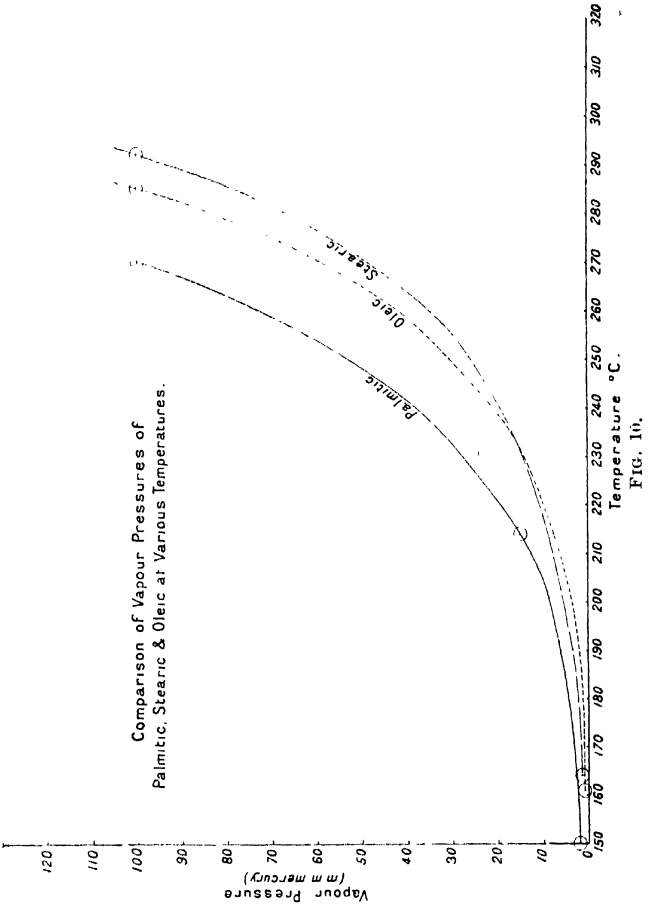


FIG. 10.

ness of the action and the failure to attain complete saponification, has been but little employed. Recently attempts have been made in Germany on an experimental scale to utilise the pancreatic

enzyme great quantities of which are available as a by-product of the slaughter houses but up to the present the process has not been conducted on a commercial basis so far as the author is aware.

The fatty acids prepared by any of the above-mentioned methods vary in colour from yellowish-white to dark brown, the intensity of the colour depending on the quality of raw fats and the method of saponification employed. Particularly in the case of recovered oils and alkali fats from the refining of cotton seed oil the fatty acids are of very bad colour.

Although it is possible to some extent to bleach the acids by filtration through charcoal or treatment with oxidising solutions, it is found much more satisfactory in practice to purify them by distillation.

It has already been stated that, unlike the glycerides which cannot be distilled undecomposed, the free acids readily distil in a current of superheated steam.

Palmitic acid distils readily in a current of steam at 170°—180° C., oleic at 200°—210° C., and stearic at 220°—230° C., and the diagram (Fig. 10) shows the variation of the vapour tensions of these important acids with the temperature.

The relative quantity of steam and fatty acid vapours which pass to the condensers varies with the vapour tension of the latter, and the higher the temperature at which the distillation is conducted the more fatty acid found in unit volume of the distillate. For example, it is found that at a temperature of 200°—220° C., 7 parts by weight of water pass into the receivers for every 1 part of fatty acids, whereas if the distillation be conducted over 300° C. about equal quantities of water and acid are obtained.

The colour of the distillates becomes gradually darker as the temperature of distillation rises, those going over below 280° C. being quite pale, while at higher temperatures darkening occurs. The 320° C. and over distillates are usually blackish-brown.

This blackening may be minimised by distilling with superheated steam in a partial vacuum, when the operation can be conducted at a lower temperature, and this method is com-

mercially successful for the distillation of the high boiling fractions. The usual practice is to distil at atmospheric pressure until the distillates become dark, and then to finish the distillation by the aid of a vacuum in either the same apparatus or a separate plant. (Still returns.)

In any case slight decomposition of the fatty acids, and particularly of any traces of unsaponified fat, occurs at high temperature with the formation of hydrocarbons, some of which distil over and are found in the distillates, but the bulk polymerise and form a non-volatile tar in the still, which is subsequently run off and sold as stearine pitch.

Stearine pitch is a black mass varying somewhat in consistency according to the amount of volatile matter left in it. It consists on the average of about 80 to 90 per cent. of solid hydrocarbons, formed by destructive distillation of the fatty acids and 10 per cent. of a mixture of neutral fat, fatty acids, and other decomposition products, the presence of which serve to distinguish it readily from petroleum and coal-tar pitches.

When the raw fatty acids contain no unsaponified fat, it is possible to obtain by careful distillation as much as 97 to 98 per cent. of pure acids, but if much neutral fat is present in the crude materials much smaller yields of acids are obtained, and a considerable quantity of hydrocarbons formed by the destructive distillation of the fat pass over. It is therefore best practice to treat the raw fat by the mixed process (viz., autoclave and then sulphuric acid), in order to reduce the quantity of neutral fat in the crude acids to a minimum.

This is well illustrated by a comparison of the yields obtained from palm oil and tallow by distillation of acids, prepared (1) by autoclaving only, (2) by autoclave followed by sulphuric (Kassler, quoted by Lewkowitsch), where it will be seen that the yield of pure acids is always higher and pitch lower when small amounts of neutral fat, which have escaped hydrolysis in the autoclave, are subsequently saponified by sulphuric treatment.

Comparison of yields from fatty acids prepared by (1) autoclaving only, and (2) autoclaving followed by sulphuric treatment. (See table on p. 176.)

Acids from	Quantity Distilled.	Duration of Distillation.	Distillate for Pressing.	Still Returns.	Stearine Pitch.
Tallow I. . .	5 tons	36 hours	94·2	2·3	3·5
„ II.. .	5 „	34 „	94·8	2·0	3·2
Bone Fats I. .	5 „	38 „	91·5	5·0	3·5
„ „ II. .	5 „	35 „	92·8	4·2	3·0
Palm Oils I. .	5 „	37 „	91·3	4·5	4·2
„ „ II. .	5 „	36 „	91·6	4·6	3·8

It will be seen from the curve (p. 173) that oleic and stearic acids have very similar vapour pressures at the temperatures of distillation, as a result of which they tend to come off together after the bulk of the palmitic and lower acids have been removed. This explains how it happens that the melting point is not lowered until the last few hours of the distillation, the tendency of the oleic to soften the distillate being counteracted by the increased percentage of stearic passing over. As the temperature rises, however, the hydrocarbons formed by decomposition of the fat come over, and the melting point is accordingly lowered, as the table of observations made by Kassler shows.

Distillation of autoclaved and acidified tallow fatty acids (Kassler):—

Sample taken after 5 hours.	Solidifying Point, ° C.	Oleic and Isoleic Acids.
5 hours	41·7	33·1
10 „	42·7	36·1
15 „	43·5	38·8
20 „	45·0	41·3
25 „	42·7	42·5

From the foregoing theoretical considerations it will be

gathered that the best conditions for distillation are only attained by careful attention to the following details:—

(1) To completely saponify the fat, leaving, if possible, no neutral glycerides mixed with the acids.

(2) To distil at as low a temperature as possible, preferably with the aid of vacuum.

(3) To avoid condensation in the dome of the still-head, and so prevent decomposition of any acids which might thus fall back into the hot mass.

No efficient separation of the individual acids is possible by steam distillation, and as a rule no attempt is made to collect various fractions in separate receivers as is done in the case of petroleum. It is true that the lower acids may be to some extent separated from those of higher molecular weight, but as a practical matter this is of little moment. Of far greater importance is the separation of the liquid oleic from the solid palmitic and stearic acids, and, as we have seen, this is not commercially possible by simple distillation. The most satisfactory method of effecting this is to distil the whole mass over and then subject the mixed distillate to pressure, whereby the liquid acids are removed from the solid, yielding on the one hand commercial oleines and on the other stearines.

The complete series of operations performed in the candleworks or by oleine and stearine makers consists, therefore, in

(1) Saponifying the fatty raw material;

(2) Distilling the fatty acids;

(3) Pressing the distillate to separate liquid oleic (oleines) from solid stearic and palmitic (stearines).

The solid cake of crude acids which floats on the top of the water in the receiver is melted and clarified and then run into shallow trays and allowed to cool slowly. It is important to avoid rapid chilling of the acids because of the tendency of the whole mass to become an amorphous mixture which cannot be separated by pressure. Slow cooling causes definite crystals of solid acids to separate, whereby efficient separation of the liquid portion is attained.

The solid cake is first pressed in the cold, when most of the oleic runs out, leaving in the press a cake which may be

warmed up a little and again pressed to remove a further quantity of oleine.

By careful pressing all the colouring matter of the distillate (iron soaps, decomposition products, etc.) passes away with the oleine, to which it imparts a colour varying from light to dark red. Hence the name "red oil" which is frequently applied to expressed oleine. The red oil from the hot press sometimes contains notable amounts of solid acids, which may be removed by cooling and re-pressing. The stearine remaining behind in

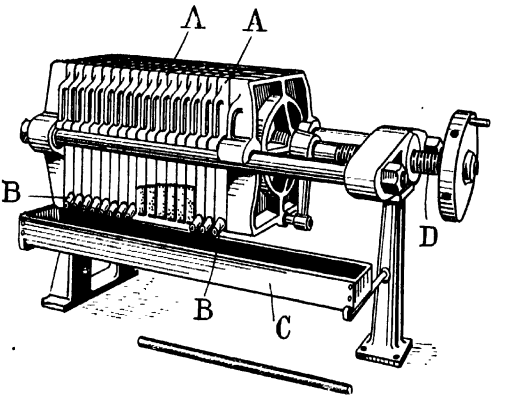


FIG. 11.—Hand Press for separating Stearine from Oleine. AA, filter plates; BB, outlet for the expressed oleine; C, collecting trough; D, worm for squeezing the plates together.

the press is of much better colour, and when sound fats have been employed it is a pure white product, but those qualities which are obtained from refuse or recovered fats are generally of a yellowish tint.

The efficiency of the separation is best determined by noting the solidifying point of the press cake. The stearine obtained when the fats have been saponified by sulphuric contains isoleic in part, which absorbs iodine and so would upset the calculation of the percentage of oleic in the cake by determination of the iodine value.

The average yield of various products obtained from tallow on

saponifying by the mixed process, followed by distillation and pressing, is:—

Solid candle material (Palmitic, stearic and oleic) . . .	60 to 64 per cent.
Oleine.	30 to 32 „ „
Pitch	2 to 3 „ „
Crude glycerine of sp. gr. 1·24 .	9 to 10 „ „

The products obtained in the above-described way are designated "distillation stearine," "distillation oleine," and "distillation glycerine."

When the saponification products are of good colour, it is sometimes unnecessary to distil them, in which case the mixture of acids is pressed right away, and the fractions are then called "saponification" stearines, oleines and glycerines, as distinguished from the distilled substances.

Saponification stearine is usually much darker in colour than the distilled product. The former has a higher melting point, and owing to the absence of isoleic acid shows a much lower iodine figure than the latter. The iodine value of saponification stearine rarely rises above 10 per cent., while distillation stearine absorbs from 20 to 30 per cent. of iodine. In good quality stearines, however prepared, the unsaponifiable matter should not exceed 1 per cent.

Saponification oleine is dark-coloured, and always contains some neutral fat, while distillation oleine is pale, and may be even white, but it invariably contains unsaponifiable matter because all the hydrocarbons formed by distillation pass out in the liquid oleine. Distillation oleine can, however, be prepared containing as much as 99 per cent. saponifiable matter by using perfectly saponified raw material and distilling with a plentiful supply of steam. The colour is still further improved by redistilling.

The alkali foots thrown down in the refining of cottonseed and other oils contains fat and fatty acids, which may be recovered by acid saponification and distillation.

Cottonseed black grease, which contains about 90 per cent. of a mixture of fat and fatty acids combined as sodium soaps, yields a

distillate from which, by pressing, stearines and oleines are prepared. Cottonseed stearines, from black grease, known in commerce as "white greases," are usually of excellent colour and contain 98 to 99 per cent. of fatty acids, with a titer test varying from 40°–43° C.

Stearines find their application chiefly in the manufacture of candles; the better qualities of oleine are used in soap-making, but if the percentage of unsaponifiable matter is high they are unfit for domestic soaps, and are then employed for textile soaps and lubricating greases.

The distillation process is also applied with great success to the preparation of marketable products from all kinds of waste and recovered fats, oils and waxes.

An important branch of the industry is concerned with the distillation of wool-scouring grease.

The brown grease, consisting of soaps and neutral waxes and alcohols, is treated with acid to decompose the soaps and the mixture of acids, etc., distilled in steam. The bulk of the free acids and alcohols distil over undecomposed, but most of the esters break up into acids and hydrocarbons which are found in the distillate.

$$C_nH_{2n+1}COOC_nH_{2n+1} \longrightarrow C_nH_{2n+1}COOH + C_nH_{2n}$$
ester

On subsequently pressing, the bulk of the hydrocarbons, which belong to the unsaturated series, pass into the oleine, which therefore frequently contains 20 to 30 per cent. of unsaponifiable matter. The stearine cake contains some of the undecomposed alcohols and solid esters, and, on the average, about 80 to 85 per cent. of acids.

The oleine is used almost exclusively in the textile soap and lubricating greasemaking, the stearine finds a market as sizing tallow substitutes, and better qualities may be mixed with soap and candle raw material.

CHAPTER XI

CANDLE MANUFACTURE—SOAP MAKING—GLYCERINE

Candle Manufacture.

THE raw materials of the modern candle industry are stearines, paraffin wax and ozokerite, and various waxes of animal and vegetable origin.

The former constitute by far the greater part of candle raw materials, the latter being only used as a general rule in small quantities for stiffening purposes.

The art of candle-making from the chemical standpoint lies in making mixtures of these products of the required degree of purity, melting point and rigidity, and, further, of producing the correct crystallisation of the stearine, etc., in the finished candle.

In the first place, the presence of impurities of an inorganic nature in the fat seriously interferes with the efficiency of a candle by affecting the capillary properties of the wick just in the same way as in the case of illuminating oils burnt in a lamp.

The melting point of the material is of course of primary importance, since if it be too low the candle tends to bend and "gutter," while too high a temperature of fusion causes a cup to form round the burning wick. The rigidity, however, is not entirely dependent upon the melting point, for it is observed that candles made from pure paraffin wax (melting point 50° C.) tend to bend and twist more readily than those from stearine of similar melting point. This is due to the smaller range of "softening" temperature of the latter substance consequent upon its greater chemical homogeneity and crystalline structure.

Further, it is found that the addition of 10 to 20 per cent. of stearine to paraffin wax gives a much firmer and more rigid product, notwithstanding the fact that the melting point of the mixture is lower than that of the paraffin. Thus a mixture of 80 per cent. paraffin wax (melting point 120° F.) with 20 per cent.

stearine of melting point 128° F. was found to melt at 115·5° F., but the mixture was much firmer at 95° F. than the wax.

Such mixtures of paraffin wax and stearine are largely used in the manufacture of candles, the relative proportions being adjusted according to the country in which they are intended to be used.

The melting point and other properties of such mixtures cannot be foretold, but must be previously determined for each case in the laboratory.

The better qualities of candles are made from stearine, or mixtures of stearine and paraffin, with carnauba wax, beeswax, ozokerite, ceresin, spermaceti, etc., all of which substances, while conferring better rigidity, also impart a finer appearance and greater immunity from "guttering" to the candle.

The relatively small proportions of vegetable or animal wax appear to produce these results in large measure by preventing the formation of large crystalline aggregates, or as it is called in technical parlance, "breaking the grain." If it be desired to colour the candle, the colour-stuff (coal-tar dyes) must be dissolved in the stearine before mixing with the wax, because the dyestuffs are insoluble in the latter.

Candles made from pure spermaceti give a good regular light, and have been accordingly chosen as the standard for the comparison of illuminating powers, the standard candle being taken as that which burns 120 grains of spermaceti per hour.

Candles made from pure beeswax show rather less consumption of candle material per hour than stearine or paraffin products.

The manufacture of the wick is also of great importance, considerable variation in the tightness of the plait being necessary with different mixtures.

The beeswax and spermaceti candle requires in general a looser wick than the stearine, while tightly-woven plaits are used with paraffin wax. The wick is made in specially constructed machines which give it a tendency to bend over in order that the used up end shall project into the side of the flame where combustion is complete, and so be continuously consumed, whereby the necessity for frequent "snuffing" is obviated.

Before use the wick is pickled by immersion in solutions of boric acid, sal ammoniac, etc., to prevent too rapid burning,

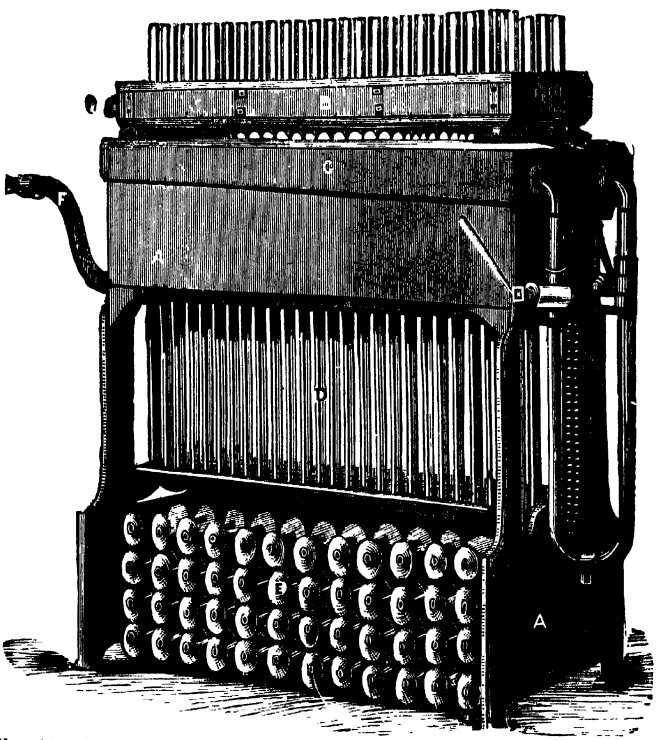


FIG. 12.—Candle-Moulding Machine (by permission of Messrs. E. Cowles). A, main body of the stand; B, movable clamps with tip bars; C, handle of the eccentric wedge; D, the pistons, having the tip moulds at the upper ends, which exactly fit the lower end of the main moulds; E, the spools, having pins on which the spools revolve; F, the crank for raising the pistons.

and to avoid accumulation of mineral matter by forming a fusible ash.

Formerly candles were made by pouring the molten mixture of stearines and waxes over the wick, but nowadays the moulding process is exclusively in vogue.

The candle machine (Fig. 12) consists essentially of a number of

water-jacketed cylinders provided with pistons operated by a crank. The wick, contained on spools, is threaded through a small hole in the piston and passed up the cylinder and held axially by a clip, or, when the machine has been started, by the previously drawn candles. The molten mass is poured into the moulds and its solidification controlled by circulating hot or cold water round the cylinders.

With stearine or stearine and wax mixtures the best results are obtained by keeping the moulds warm and allowing crystallisation to proceed rather slowly; but paraffin wax requires, on the contrary, to be first heated to a high temperature and then rapidly chilled by passing cold water through the jacket, the object of this variation in treatment being in all cases to produce a homogeneous crystalline system, showing the minimum of large aggregates or "grain."

Soap Making.

When the saponifiable oils and fats are boiled with concentrated solutions of caustic alkalis, the glycerides are hydrolysed, glycerol is liberated, and the fatty acids combine with the alkali and a portion of the water forming soaps. The term "soap" in an industrial sense is applied to what is really a mixture of alkali salts of the higher fatty acids, water, and frequently inorganic salts or mineral matter, and is quite a different product to the anhydrous salts of the fatty acids which are sometimes called soaps by the chemist.

The hardness of a soap varies with the composition of the oil or fat from which it was made, and also with the alkali: the sodium soap from any given oil being always harder than the soap made from the same oil by caustic potash. Further, the soaps formed by the unsaturated acids are much softer than those of the saturated series. It is usual, therefore, to call the sodium soaps made from fats or mixtures of fats and semi- or non-drying oils "hard" soaps, as distinguished from the potash compounds of the drying oils or "soft" soaps.

Practically all the saponifiable oils and fats can be used as raw material for soap-making, the art of the manufacturer consisting in blending the various oils and fats at his disposal to obtain a soap of suitable properties.

Rosin, which contains as much as 80 per cent. of free acids, may be mixed with the oils for saponification, and the molten soap paste is usually churned up with mineral matter, lime, talc, silicate of soda, etc. (fillers), for the preparation of hard soaps.

Hard Soaps.—Two methods are employed for the preparation of domestic soaps, viz.:

(1) The cold process.

(2) The hot process.

In the cold process, the molten fat is vigorously churned up with the requisite quantity of alkali dissolved in as much water as is necessary to impart to the soap the desired hardness and solubility. In a few minutes the mass commences to thicken, and at this point it is quickly poured into frames, covered up and allowed to stand for twenty-four to thirty-six hours, at the end of which time saponification has reached a maximum, and the soap may be cut into slabs.

This process can only be carried out satisfactorily on coconut oil or tallow mixed with small amounts of other oils, and it is essential that the fatty mixture contains but a small amount of free acids, which combine with the alkali too rapidly, and so form lumps in the soap.

When an acid is neutralised by a base heat is evolved, and this explains how it is that some fats can be saponified without the aid of external heat. The free fatty acids always present in the oil combine with the alkali, whereby heat is given out, but as the reacting bodies are surrounded by layers of oil and alkali, this heat cannot get away, and it is dissipated by heating up the emulsified layers of liquor and oil in the immediate neighbourhood. The temperature is thus brought high enough to saponify this layer, which in turn emits heat, and so the whole mass is converted into soap.

As saponification proceeds, greater masses react, the heat evolution is increased, and so the reaction proceeds faster and faster until the equilibrium point is approached, when the velocity slows down again and ceases altogether when about 97 per cent. of the fat is converted into soap.

For this reason soaps made by the cold process always contain small amounts of free alkali, which is more or less obnoxious.

For the preparation of neutral soaps recourse must be had to the hot process, which is carried out in the following way:—

The oils are placed in a large iron pan (soap kettle) provided with a perforated steam coil; steam is blown in until the oil is heated to about 80° C. and a quantity of water from the condensed steam has formed at the bottom.

Caustic soda is then gradually added, while the contents of the pan are kept in a state of ebullition by means of the jet of live steam. The strength of the caustic solution (lyes) and the quantity added from time to time is determined by the nature of the oils and the amount of water originally present. At the outset the lyes must be added slowly until saponification is well under way, when it may be added more rapidly, the heat of saponification and neutralisation of the oils and fatty acids greatly assisting the velocity of the action. If the alkaline liquor be allowed to become too strong, the soap paste is "cut" into "curds" upon which the alkali cannot satisfactorily act. The correct concentration is ascertained by taking a small sample from the pan from time to time and placing a little on the tongue, when the "strength" of the alkali can be felt.

After the calculated amount of caustic has been added the pasty solution of soap is boiled up and a saturated solution of common salt added, little by little, to "throw out" the soap (graining). The contents of the kettle are then allowed to stand, when the saline liquor containing the glycerine separates out and the curdy granules of soap float on the top. The liquor is next withdrawn and run into tanks for the recovery of glycerine contained in it.

Steam is then blown through the soap curd until the water of condensation causes the granules to swell up and fuse together, or "close" as it is called. More alkali is now boiled in to ensure complete saponification of any remaining traces of fat (strengthening change) after which the soap solution is just "opened" again with salt.

At this stage it is important to adjust the quantity of salt carefully until the soap just "opens," but is not unduly grained. After a further stand for a few hours the liquor which falls to the bottom is again drawn off and the curd just closed with steam. The contents of the pan are then well covered up to keep the

heat in and allowed to stand for twenty-four to forty-eight hours, according to the size of the charge. This is called the "settling" process.

During this settling the contents of the pan separate into three layers, the top consisting of good molten soap (neat soap or goods), the intermediate is a slimy soap much richer in water (nigers), and the excess of liquor at the bottom.

The top layer of neat soap is skimmed off and placed in frames to cool and solidify. The nigers are run into another pan to be further treated.

The metallic soaps and other impurities are found in the intermediate layer, which is usually of a dark or blackish colour, hence the term "nigers."

The composition of the three layers is as follows:—

	Water.	Anhydrous soap.	Salt and free alkali.
Top layer (neat soap)	30 to 35 per cent.	63 to 68	0·5 to 1 per cent.
Intermediate layer (nigers)	55 to 65 „	35 to 45	1·5 to 3·0 „
Under layer (liquor)	95 to 97 „	nil	3·0 to 5·0 „

The composition of these three layers remains fairly constant between these limits, but varies slightly with the nature of the oils, the temperature and pressure at which the soap solution is settled, and the composition of the salts and alkalis present.

The top layer of neat soap never contains more than 68 to 70 per cent. of anhydrous soap, and the explanation of this phenomenon has provoked much discussion.

Lewkowitsch some years ago suggested the term "water of constitution" for the 30 to 35 per cent. of water always present.

On this view commercial soap may be conceived as a kind of "crystalline" compound containing a definite amount of "water of crystallisation."

More recently, however, the conceptions of colloid chemistry

and phase rule have been invoked to explain the rationale of the soap-making process. As this view is of considerable importance in showing the application of recent scientific discoveries to oil chemistry, it will be of interest to consider it at length.

If to a given bulk of water ether be added drop by drop it is found that up to a certain point the ether dissolves in the water, forming a homogeneous solution. At a certain concentration, however, any further ether added refuses to dissolve in the water but floats upon the top as a separate layer. The mixture now is a heterogeneous system consisting of two layers, the lower being water containing a little ether in solution, the upper, ether containing water in solution. These two layers are called phases, and their composition is independent of the absolute amount of ether present, but varies with the temperature and pressure. This variation, and the circumstances which control it, may be indicated by the phase rule discovered by Willard Gibbs, who has represented the problem in the form of an equation.

$$F = (C + 2) - P,$$

where P, F and C are number of phases, degrees of freedom, and components respectively. The meaning of the expression "degrees of freedom" will be gathered by considering the illustration given above. Clearly there are two phases, the ether layer and the water layer, and also two components, viz., water and ether. Substituting in the equation we get

$$F = (2 + 2) - 2$$
$$= 2$$

i.e., the system possesses two degrees of freedom. This means that if two conditions under which the system exists be fixed, the equilibrium is also fixed. At constant temperature and constant pressure the composition of both liquid layers of the water-ether system remains unalterable, but if the temperature be changed, either the pressure must change with it or the composition of the phases will be readjusted to meet the changed conditions. This is in no wise dependent upon the absolute quantities of the two constituents.

Consider now the mass in the soap kettle. At the conclusion

of the graining process it consists in its simplest form of two phases, soap poor in water and water rich in salt.

For the moment we may postulate the presence of only three components, viz., water, salt, and anhydrous soap. Applying the phase rule the system must have three degrees of freedom. If the temperature and pressure be fixed, the composition of the two phases can vary according to the concentrations of the three components present. If, however, these concentrations are also fixed, the composition of the phases is unalterable. This, however, is an abstract case, for in practice we may have an immense number of components, water, salt, soap, caustic soda, alkali, carbonates and glycerine. This would give us six components, and if the mass were treated in such a way that two phases only formed, the phase rule says that the system can have no less than six degrees of freedom. Now the temperature and pressure of soap-boiling operations may be taken as constant (viz., 100° C. and atmospheric), and this leaves us with four conditions to fulfil before the composition of the phases becomes fixed; these conditions are the concentrations of the various components, an alteration of any one of which must affect the composition of the soap and aqueous layers. This serves to show the complexity of the problem, but the study is still more involved, since soap behaves as a colloid.

Viewed by the ultra-microscope, soap solutions are found to consist of minute particles of soap (microns) suspended in the water, the individual particles being of course so small as to be outside the limit of ordinary microscopic vision, and the solution is consequently quite clear to the naked eye.

The particles in a colloidal solution are held in suspension by capillary forces which act between the particle and liquid in which it is suspended.

Let us consider the simplest case of a pure substance, *e.g.*, soap suspended in pure water. It can be shown that if the surface tension between the particle and liquid is lowered by the addition of the electrolyte the latter tends to concentrate round the particles.

This phenomenon is known as "adsorption."

Now the colloidal particle of soap is in equilibrium with the

water which surrounds it, but if we add salt to the "solution," the salt distributes itself, part adsorbing on the particles and part dissolving in the water. This results in a change of equilibrium, and if sufficient salt or other electrolyte is added the equilibrium becomes so upset that the particle can no longer remain in suspension, but separates itself from the liquid in the form of a precipitate (coagulation). In all cases a certain minimum quantity of electrolyte is necessary to effect the coagulation, depending on the original stability of the colloid and the nature of the electrolyte.

The precipitated particle contains adsorbed water and electrolyte, and its composition is dependent upon four factors.

(1) The nature and structure of the colloid particle.

(2) The nature of the suspending liquid.

(3) The nature of the electrolyte.

(4) The temperature.

We are now in a position to appreciate the interpretation put upon the various soap-boiling operations by Merklin :—

The saponified oils present in the first case a pasty mass of soap solution, in which free alkali, glycerine, etc., is dissolved.

To this is added salt solution until the soap is coagulated, and from the application of the phase rule we see that the composition of the two phases (liquor and soap granules) will depend upon the temperature and pressure and concentrations of the compounds present. The liquor is a solution of the electrolytes and glycerol, while the curd is an adsorption product of salt, water and soap, the relative proportions of which will depend not only on the above factors, but also on the nature and structure of the colloid itself, *i.e.*, the fatty acids of the soap, the nature of the electrolytes, etc.

In the fitting operation the soap curd is partially closed by water and allowed to stand, when it separates into two layers (phases), both possessing the same constituents, but in varying proportion, just as in the case of the system ether-water.

The upper consists of a phase rich in soap and poor in water, the lower poor in soap but rich in water, both being colloidal solutions of anhydrous soap in salt solutions of variable composition according as the factors mentioned above are altered.

The formation of the third or bottom layer of liquor is an accidental occurrence due to cooling of the soap, and is in no way essential to the settling process. Lewkowitsch has shown, in fact, that if the pan be sufficiently protected from heat losses no third layer forms.

Merklin has made soap from a large number of oils, and obtained very satisfactory evidence in support of his theory. The wide differences in behaviour towards "salting out" manifested by different types of oil are readily explicable when one remembers the marked influence of lower members of the fatty acid series on surface tension relations which result in soaps of very diverse colloidal character.

Toilet Soaps.

The best qualities of toilet soap are made by drying a settled soap made from good quality fats, disintegrating the soap in a machine where it is mixed with colours and perfumes, and finally forcing the finely-divided milled soap through a mould by pressure. Machines for this purpose are called plodders. A toilet soap should contain no free alkali. This is attained by using a soap of minimum alkalinity and adding to it in the mill weakly acid substances, such as glue perfumes, colours, etc.

A number of special soaps are nowadays made by incorporating various materials with pulverised soap in the mill or crushing in the molten paste. The description of these falls outside the scope of the present work (disinfecting, transparent, petroleum and other soaps).

Detergent Action of Soap.

The explanation of the detergent action of soap solutions has been much discussed, but our knowledge on the subject has been considerably extended by the experiments of W. Spring.

The removal of fatty impurities from cloth and other objects may be explained by the powerful emulsifying action of the soap, but this does not account for the abstraction of dirt from the materials. Spring has studied the properties of suspensions of lampblack in soap solutions. He finds that the rate of deposition of lampblack from soap solutions varies with the concen-

tration of the soap. Perfectly pure lampblack is deposited from pure water almost immediately, but 1 part of alkali in 6,000,000,000 parts of water sensibly retards the rate of deposition, and 0·5 per cent. of soap dissolved in the water keeps the black in suspension for ten days.

Further, when water containing lampblack in suspension is filtered, all the lampblack remains on the paper, but when a soap solution having lampblack in suspension is filtered, the paper is not even blackened, hence the carbon must have formed a colloidal combination with the soap.

The soap solution from which lampblack has been deposited contains more ash than the original solution. Hence lampblack causes decomposition of soap into acid and basic soap, agglutinates

$$2R.COONa + H_2O \longrightarrow \underbrace{R.COONa} + \underbrace{NaOH} + RCOOH$$

with the former, leaving a larger portion of basic in solution. The probability of carbon combining with the acid soap is strengthened by the observation that they are of opposite electrical polarity.

When lampblack in water containing a trace of alkali is submitted to electrical cataphoresis the black is deposited on the cathode, while a soap solution forms a deposit on the anode, containing a smaller proportion of ash than that left in solution, indicating its acid nature. Hence from this the cleansing action of soap is an example of substitution:—$OD + S = D.S. + O$

O = object defiled by dirt $D.$ $S.$ = soap, both $O.D.$ and $D.S.$ being colloidal adsorption compounds.

The lack of cleansing power of alcoholic soap solutions is explained by the fact that in alcoholic solution soap is not decomposed into acid and basic parts."

Briefly, on this view, soap cleanses by hydrolysing into acid and basic parts which are capable of entering into colloidal combination with the dirt, and consequently removing the latter at the same time as the soap is removed on washing with water.

THE RECOVERY OF GLYCERINE.

Glycerine is a by-product obtained from the saponification of fats and oils in the candle and soap works.

The quantity of glycerine obtainable from the liquors varies according to the quality of the fat and the method of saponification. The lime saponification and autoclave processes yield a glycerine lye of comparative purity, while the acidification and Twitchell processes produce liquors highly charged with impurities. Glycerine solutions obtained from the soap pan vary widely in the amount of impurity contained in them, the quantity depending on the nature of the fats and alkalies employed in the process. The operations entailed in the preparation of glycerine from whatever source consist in:

(1) Removal of the organic impurities.

(2) Removal of the water and inorganic salts by evaporation and crystallisation.

(3) Purification of the crude glycerine so obtained by distillation *in vacuo*.

The product obtained from one distillation varies from pale yellow to brown in colour; it is fairly pure and finds application in the manufacture of explosives. It is known as "dynamite glycerine."

On submitting dynamite glycerine to further distillation a product of great purity is obtained, known as "pure glycerine."

As illustrating the principles involved it will be sufficient to describe the production of these commercial glycerines from soap lyes. Soap lye is a dirty brownish liquor containing caustic soda, common salt, carbonates and sulphates of soda, soap (particularly the salts of the lower fatty acids which are soluble in a salt solution), and organic albuminous and colouring matters from the fats. The liquor usually contains from 4 to 5 per cent. of anhydrous glycerol.

To remove the fatty and organic impurities the liquor is heated by steam coils, and HCl added until the solution is only

faintly alkaline. A solution of alum is then poured into the hot liquid when the following reactions take place:

$$6\ R{\cdot}COONa + Al_2(SO_4)_3 \longrightarrow 2\ (R{\cdot}COO)_3Al + 3Na_2SO_4$$

soluble soap — insoluble soap

$$6\ NaOH + Al_2(SO_4)_3 \longrightarrow 2\ Al(OH)_3 + 3\ Na_2SO_4$$

insoluble

The soluble soaps are converted into insoluble aluminium soaps, and a portion of the alum is simultaneously decomposed by the free alkali present into insoluble gelatinous aluminium hydroxide which "adsorbs" the albuminous matter and colour-stuffs and so precipitates them. This again is an example of colloidal precipitation. The excess alum is now precipitated by addition of caustic, and the carefully neutralised suspension passed through a filter press, when a clear liquid is obtained containing sulphates, chlorides and carbonates of soda, and small traces of other impurities mixed with the glycerol solution. The aqueous liquid is concentrated *in vacuo* till a gravity of 1·24 corresponding to 80 to 85 per cent. glycerol is attained. This concentration is usually carried out in three stages, the first yielding a solution containing about 40 per cent. of glycerol, the second about 75 to 80 per cent. glycerol. The bulk of the salt crystallises out in the first stage and is removed and freed from adhering traces of glycerol by steaming. The final crude product contains about 80 to 85 per cent. anhydrous glycerol, 10 per cent. water, and 10 per cent. salt.

In order to remove the salt and water and to further purify the glycerine it is distilled *in vacuo*. The Scott patent, of which a diagram is shown, is the plant usually employed. The distillation is effected by steam superheated to about 160° C., the degree of superheat being regulated by a specially constructed damper.

From saponification-glycerine the Scott patent produces pure glycerine in one distillation, while soap-makers' crude yields "dynamite" glycerine in one, and "pure" glycerine in two, distillations. The loss in distillation may be reduced as low as 2 per cent. The distilled glycerine may be further decolorised by treatment with charcoal.

Vast quantities of dynamite glycerine are used for the manu-

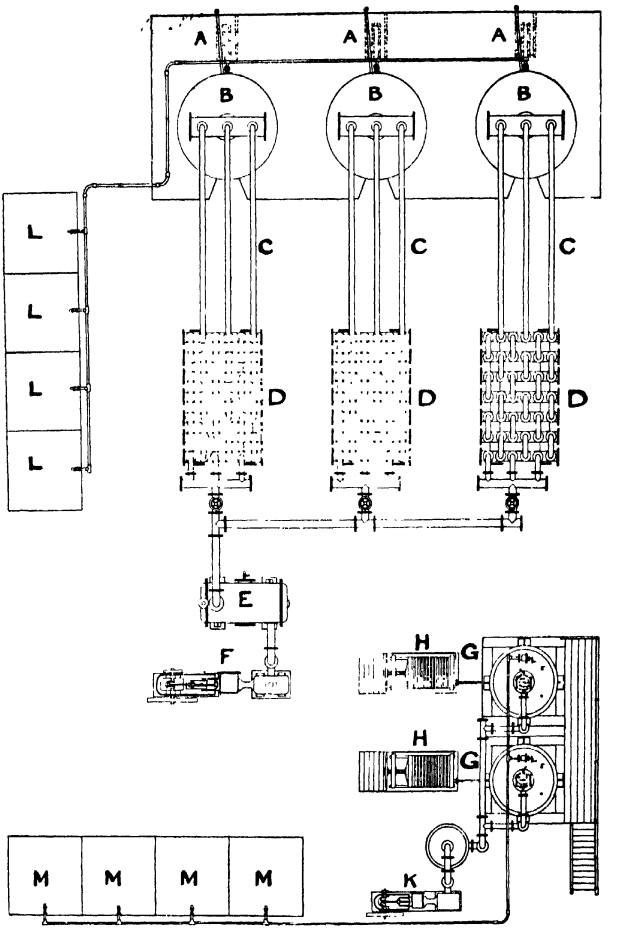


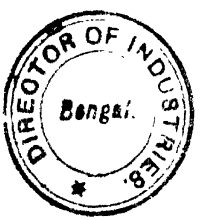
FIG. 13. The Scott Patent Glycerine Distillation Plant (by permission of Messrs Geo. Scott (London), Ltd.). L, storage tanks for crude glycerine; B, cylindrical stills; C, pipes leading vapours to the condensers D; E, F, K, vacuum pumps; M, treatment tanks for distilled glycerine; H, filter presses for removal of the charcoal; G, concentrators; A, steam and glycerine inlet pipes.

facture of nitro-glycerine. It is a yellowish-coloured viscous liquid of specific gravity 1·261 at $\frac{20^{\circ}}{4}$ C.

For the preparation of explosives the product must be free from organic impurities and contain not more than 6 per cent. of water and traces of salts.

If the distillation has not been conducted with sufficient care, polyglycerols are formed, and the presence of these substances in any quantity renders the glycerine unfit for the preparation of explosives.

"Pure" glycerine is a viscous colourless liquid containing only 1 to 2 per cent. of water. It is employed in medicine, and to a limited extent in the preservation of fruit.



CONCLUSION.

Scientific and Technical Research on Problems in the Oil and related Industries.—In the preceding pages an attempt has been made to present to the reader an outline of the methods employed in obtaining, purifying, and preparing finished products from oils and fats, with particular reference to the applications of chemical principles; and from a study of this brief sketch it will be gathered that although an immense amount of information has been accumulated during recent years on the chemistry and physics of the industry, our knowledge in many departments still stands greatly in need of enlargement, and a fertile field is offered not only to the pure chemist, but also to the chemical technologist in the origination of better and more economical processes of refining, and in the utilisation of oil products for a great variety of purposes. It will, therefore, not be without interest to review briefly the direction in which investigation is proceeding and may advance in a few typical departments.

Petroleum.—The transformation of hydrocarbons into homologues of lower molecular weight and boiling point, and the reverse synthesis of viscous oils of high carbon content from lower members, presents a fascinating study in organic and physical chemistry. The demands for petroleum motor-spirit will probably outgrow the production within the next few years, since the percentage of this volatile fraction which can be obtained by simple distillation from the crude amounts to only a few per cents., while on the other hand, vast quantities of residuum, notably in the Russian fields, have hitherto found a market only for fuel at comparatively low prices. Now it has been shown that by subjecting the hydrocarbons boiling above 300° C. to destructive distillation, a certain proportion of low boiling products can be obtained, and, as we have seen, this process has achieved commercial success for the preparation of illuminating oil. Further, by careful regulation of the temperature at which "cracking" takes place, small percentages of the

more volatile substances can be obtained, but the yield up to the present is too small to make the process remunerative, the bulk of the oil being converted into less valuable products, coke, etc. There seems, however, no reason why this yield should not be increased and the development of the reaction on a technical scale comes within the province of chemistry. The reverse process would seem to have less interest at the moment, but its possibility has been shown by Engler who has been able to produce thick viscous oils of high molecular weight from amylene by polymerisation in the cold in the presence of aluminium chloride. The commercial importance of these theoretical possibilities cannot be foretold, since the market for petroleum products changes year by year with the progress of engineering invention,—the volatile naphthas, thirty years ago almost a waste product, being more valuable to-day than the heavier fractions. At any rate, the ability to transform the homologous mixtures on a practical scale in either direction at will would unquestionably have a far-reaching effect on the industry.

Apart from this, in petroleum we have a plentiful supply of hydrocarbons of all types, and, since these form the parents of the organic compounds, it should be possible to use them as raw materials for the preparation of a host of substances. The fact that the aromatic or benzene derivatives form only a small proportion, and that the inert paraffin compounds predominate, has made the problem intensely difficult, but the naphthenes and olefines are fairly reactive, and already from them a number of ketones available in the manufacture of artificial perfumes, synthetic dyestuffs, fatty acids, etc., have been prepared by means of Grignard's reaction. Naphthenic acids from the alkali refining of petroleum have been to some slight extent employed for soap-making, and their lead and nickel salts as driers in the paint and varnish industry. Finally, the condensation products of the unsaturated hydrocarbons with aldehydes (formolites) are being studied, and may yield colloids of unique properties, valuable in the arts.

Saponifiable Oils.—Our knowledge of the exact composition as regards mixed glycerides, etc., of many oils, fats and waxes, particularly in so far as they are influenced by conditions of

growth, climate and soil, breed, race, etc., is extremely vague, and needs to be carefully studied, not only from the chemical standpoint, but also by collaboration with the agriculturist. Among the problems which have attracted attention in the treatment of the fatty oils, the deodorisation and purification of malodorous oils (fish oils, etc.), is of pre-eminent importance; the obnoxious odours are due no doubt to extremely minute quantities of impurities, the removal of which could probably be readily effected if our knowledge of their chemical nature were supplemented by extended research. Again the production of solid fats from liquid oils by reduction of the double bonds by hydrogen gas in the presence of a catalyst, has been the subject of much investigation, and still remains an inviting problem to the physical chemist.

The ignorance, both from a purely chemical and technical standpoint, as to the nature of the changes undergone by the unsaturated glycerides during oxidation and polymerisation for the production of boiled, polymerised and blown oils, has been already commented upon. These changes stand in need of more extended study by the physical chemist in order that quicker and more economical methods of preparing them may be resorted to, and by the organic chemist for the utilisation of some of the curious gelatinous masses which result from the treatment.

Soap-making.—Among all the departments of industry into which oil enters, probably the process of soap-making holds more secrets for the physical chemist than any other. The great variation in behaviour of different oils in the soap pan, according to their content in lower glycerides, has long been known, but it has been reserved for Merklin to indicate the reasons for these anomalies, and at least to form a sound basis for study. Mention has been made of this in the section on Soap-Making.

As in all branches of applied science, it is imperative for success that the investigator shall be in intimate contact with the industry and hence thoroughly conversant with its problems and needs; but at the same time a thorough grasp of the principles of pure science, with an appreciation of the importance of what in many cases may appear at first sight recondite observations, is of inestimable value. In short, the chemist engaged in industrial

research cannot be too highly versed in scientific lore so long as he learns at the same time to work forward to his definite goal undistracted for the time being by the multitude of side lines which may open to his view.

To this end he must in the first place learn to make the best possible use of the current literature, both technical and scientific. The latter may appear to be a big undertaking, but it need not be so. His knowledge of general principles will in all cases enable him to recognise the particular kind of pure scientific research which may conceivably have a bearing upon his problem; and having formulated this conception it will be found a relatively simple matter to rapidly glance through the index of treatises and journals, select the particular articles or papers which interest him, and make a note of their more important conclusions.